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THE EFFECT OF MOLAR MASS DISTRIBUTION ON SOLID STATE DEGRADATION KINETICS OF POLY (4-METHYL CATECHOL)

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Harika Topallar tarafından yüksek lisans tezi olarak sunulan "THE EFFECT OF MOLAR MASS DISTRIBUTION ON SOLID STATE DEGRADATION KINETICS OF POLY (4-METHYL CATECHOL), (POLİ (4-METİL KATEŞOL)'ÜN MOL KÜTLESİ DAĞILIMININ KATI HAL BOZUNMA KİNETİĞİ ÜZERİNE ETKİSİ)" başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 06.09.2010 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

POLİ (4-METİL KATEŞOL)'ÜN MOL KÜTLESİ DAĞILIMININ KATI HAL BOZUNMA KİNETİĞİ ÜZERİNE ETKİSİ

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Bu çalışmada 4-metil kateşol'ün oksidatif polikondensasyon reaksiyon şartları incelendi. Reaksiyonlarda oksidant olarak NaOCl, H_2O_2 ve hava oksijeni kullanıldı. Yapılan denemeler neticesinde en aktif oksidant NaOCl olarak bulundu. Ayrıca sentezlenen polimerlerin yapı ve özellikleri FT-IR, UV-Vis, ^{1}H-NMR, ^{13}C-NMR, SEC, ve TG-DTG ile karakterize edildi. Tezin son aşamasında ise mol kütlesi dağılımının, aktivasyon enerjisi, preexponansiyel faktör gibi katı hal bozunma kinetiğine ait bazı parametreler üzerine etkisi incelendi. Kinetik parametrelerin hesaplanması, özel olarak tasarlanmış WEB tabanlı PC programı ile yapıldı. Kinetik parametrelerin hesaplanmasında tek ısıtma hızına uygulanan (Coats-Redfern, Horowitz-Metzger, MacCallum-Tanner, Van Krevelen, Wanjun-Yuwen-Hen-Cunxin ve Madhusudanan-Krishnan-Ninan yöntemi) ve birden fazla ısıtma hızna uygulanan yöntemler (Flynn-Wall-Ozawa, Friedman, Tang, Kissinger-Akahira-Sunose ve Kissinger yöntemi) kullanıldı.

Elde edilen sonuçlar neticesinde, molekül ağırlığı artıkça aktivasyon enerjisinin de artığı görüldü. Ayrıca sentezlenen bütün polimerler için en uygun kinetik yöntemin MacCallum-Tanner yöntemi olduğu görüldü.

Anahtar kelimeler: 4-metil kateşol, sentez, katı hal bozunma kinetiği, kinetik yöntemler

ABSTRACT

THE EFFECT OF MOLAR MASS DISTRIBUTION ON SOLID STATE DEGRADATION KINETICS OF POLY (4-METHYL CATECHOL)

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The conditions for oxidative polycondensation reaction of 4-methyl catechol were investigated in this work. NaOCl, H_2O_2 and air oxygen were used as oxidant in the reactions. In the result of the studies, NaOCl was found as the most active oxidant. Also the structure and properties of polymers synthesized were characterized with FT-IR, UV-Vis, ^{1}H-NMR, ^{13}C-NMR and TG-DTG techniques. The effect of molar mass distribution on some parameters of solid state degradation kinetics such as activation energy, pre exponential factor were determined at the final stage of the study. Calculation of kinetic parameters was done by a webbased PC programme. Single heating rate methods (Coats-Redfern, Horowitz-Metzger, MacCallum Tanner, Van Krevelen, Wanjun-Yuwen-Hen-Cunxin, Madhusudanan-Krishnan-Ninan) and multiple heating rate methods (Flynn-Wall-Ozawa, Friedman, Tang, Kissinger-Akahira-Sunose, Kissinger) were used to calculate the kinetic parameters.

As a result, it was seen that activation energy increased with increase of molar mass and also the most suitable kinetic method was MacCallum Tanner method for all polymers.

Key words: 4-methyl catechol, synthesize, solid state degradation kinetics, kinetic methods.

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SYMBOLS AND ABBREVIATIONS

Formulas	**Explanation**
A	Preexponential factor
CR	Coats-Redfern
DMP	Dimethyl phenol
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E	Activation energy
FR	Friedman
FWO	Flynn-Wall-Ozawa
H_2O_2	Hydrogen peroxide
HM	Horowitz-Metzger
IR	Infrared
KAS	Kissinger-Akahira-Sunose
KOH	Potassium hydroxide
min	Minute
MKN	Madhusudanan-Krishnan-Ninan

SYMBOLS AND ABBREVIATIONS (CONTINUE)

Formulas	**Explanation**
mL	Mililiter
M_n	Number average molar mass
MC	Methyl catechol
MT	MacCallum-Tanner
M_w	Weight average molar mass
n	Reaction order
NaOCl	Sodium hypochloride
NMR	Nuclear magnetic resonance
O_2	Oxygen
PDI	Polydispersity index
PMC1	The polymer syntesized by NaOCl oxidant
PMC2	The polymer syntesized by H_2O_2 oxidant
PMC3	The polymer syntesized by air oxidant
q	Heating rate
R	Gas constant
$SiMe_4$	Tetramethyl silane

SYMBOLS AND ABBREVIATIONS (CONTINUE)

Formulas	**Explanation**
t	Time
T	Temperature
TG	Thermogravimetry
vK	van Krevelen
WYHC	Wanjun-Yuwen-Hen-Cunxin

1 INTRODUCTION

The majority of compounds undergo physical and chemical changes when subjected to heat. Under experimental conditions, these changes are characteristic of the substance examined, and can be used for its qualitative and quantitative analysis. For an analysis of this kind, phenomena accompanying thermal change, such as changes in temperature, weight volume and state, or changes in the physical properties of the substance (electrochemical potential, dipole moment, magnetic susceptibility, crystal structure, electric conductivity, …etc.) are suitable characteristics.

Excellent accounts of the basic, but difficult, concepts of heat and temperature and the development of temperature scales have been given by Wunderlich (1990). A detailed thermodynamic background to thermal analysis and calorimetry has been provided by Van Ekeren (1998). In very brief summary, heat is one of the forms in which energy can be transferred. Such transfer requires a temperature difference and three mechanisms of transfer have been identified: conduction, convection, and radiation.

The laws of thermodynamics deal with thermal equilibrium (zeroth), conversion of energy (first), direction of spontaneous processes including heat transfer (second), and the reference point for entropy measurements (third).

To provide useful qualitative and quantitative information on the effect of heat on materials, experiments have to be carefully planned, and often sophisticated equipment to use are required. The following formal definition of thermal analysis was originally provided by the International Confederation for Thermal Analysis and Calorimetry (ICTAC).

Previous, thermal analysis (TA) refers to a group of techniques in which a property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. A recent discussion of the above ICTAC definition by Hemminger and Sarge (1998) points out some of the difficulties and suggests some modification to:

New, thermal analysis (TA) means the analysis of a change in a property of a sample, which is related to an imposed temperature alteration. Hemminger and Sarge explain that: (a) .analysis. means much more than monitoring. ; (b) in most experiments it is a change in a property, rather than the property itself which is monitored and (c) it is the temperature of the sample's environment (e.g. a furnace), rather than the actual sample temperature which is programmed.

A temperature alteration. includes: (i) a stepwise change from one constant temperature to another; (ii) a linear rate of change of temperature; (iii) modulation of a constant or linearly changing temperature with constant frequency and amplitude; and (iv) uncontrolled heating or cooling. The direction of change may involve either heating or cooling and the above modes of operation may be combined in any sequence. Isothermal experiments, other than at ambient temperature, are included in this definition under mode (i), where the first constant temperature is usually ambient temperature and the change is to the desired isothermal experimental conditions. The temperature may also be programmed to maintain a constant of reaction, such a mode is a sample-controlled programme.

Table 1.1: Some milestones in the development of the thermal measurements (Brown,2001).

Date	**Persons**	**Developments**
1714	Fahrenheit	Mercury thermometer and temperature scale
1742	Celsius	Temperature scale
1760	Black	Ice calorimeter
-1784	Lavoisier&Laplace	-ditto-
1782	Wedgwood	Pyrometer
1822	Seebeck	Thermoelectric effect
1826	Becquerel	Thermocouple development
-1836	Pouillet	-ditto-
-1886	Le Chatelier	-ditto-
1848	Kelvin	Absolute temperature scale
1871	Siemens	Resistance thermometer
1892	Le Chatelier	Optical pyrometer
1899	Austen-Roberts	DTA
1907	Henning	Dilatometry
1915	Honda	Thermobalance

1.1 Thermoanalytical Methods

Effects produced by a change in temperature may be detected in various ways. The observation can be based on the alteration of any characteristic of the material (its weight, volume, magnetic susceptibility, …etc.) or on the change of its behaviour with respect to a given reference substance.

The thermoanalytical methods are grouped in Table 1.2 in accordance with this concept. These methods, suitable for the detection of physical and chemical changes and those making possible qualitative or quantitative evaluation are also shown.

In addition to the techniques given in Table 1.2, there are several other methods used occasionally for the investigation of the starting materials and the products of decomposition. Owing to the influence of the experimental conditions, the results of measurements made by various techniques are not always consistent, and this was one of the reasons for the slow development in the use of thermal methods.

Table 1.2: Thermoanalytical Methods (E. Brown, 2008).

Property or Physical Quantity	**Technique**	**Abbreviation(s)**	**Notes**
Heat	Calorimetry		
Temperature	Thermometry		May also be described as heating or cooling curves.
Temperature Difference	Differential Thermal Analysis	DTA	A technique where the temperature difference between a sample and reference material is measured.
Heat Flow Rate	Differantial Scanning Calorimetry	DSC	A technique where the heat flow rate difference into a sample and a reference material is measured.
Mass	Thermogravimetry or Thermogravimetric Analysis	TG TGA	The abbreviation TG has been used, but should be avoided, so that it is not confused with T_g(glass transition temperature).
Dimensional and Mechanical Properties	Dynamic Mechanical Analysis Thermomechanical Analysis Thermodilatometry	DMA TMA TD	Moduli (storage/loss) are determined. Deformations are measured. Dimensions are measured.
Electrical Propoerties	Dielectric Thermal Analysis Thermally Stimulated Current	DEA TSC	Dielectric Constant/ Dielectric Loss measured Current
Magnetic Properties	Thermomagnetometry		Often combined with TGA
Gas Flow	Evolved Gas Analysis Emanation Thermal Analysis	EGA ETA	The nature and/or amount of gas/vapour is determined. Trapped radioactive gas within the sample is released and measured.
Pressure	Thermomanometry Thermobarometry		Evolution of gas is detected by pressure change. Pressure exerted by a dense sample on the walls of a constant volume cell is studied.
Optical Properties	Thermoptometry	TL	A family of techniques in which an optical characteristic or poperty of a sample is studied. Emitted light measured.
Acoustic Properties	Thermosonimetry or Thermoacoustimetry		Techniques where the sound emitted (sonimetry) or absorbed (acoustimetry) by the sample is studied.
Structure	Thermodiffrectometry Thermospectrometry		Techniques where the compositional or chemical nature of the sample are studied.

1.1.1 Thermogravimetry (TG)

Thermogravimetry (TG) is an experimental technique in which the weight or, strictly speaking, the mass of a sample is measured as a function of sample temperature or time. The sample is typically heated at a constant heating rate (so-called dynamic measurement) or held at a constant temperature (isothermal measurement), but may also be subjected to non-linear temperature programs such as those used in sample controlled TG (so-called SCTG) experiments. The choice of temperature program will depend upon the type of information required about the sample. Additionally, the atmosphere used in the TG experiment plays an important role and can be reactive, oxidising or inert. Changes in the atmosphere during a measurement may also be made (Gabbott, 2008).

The schematic diagram for a continuous thermobalance is shown in Figure 1.1. The sample is placed into a crucible, fixed on an upward- or downward-pointing extension of the balance arm. The sample is heated by means of a programmed electric furnace, which also houses a thermocouple. With the aid of this thermocouple and a millivoltmeter, the weight of the sample can be recorded continuously as a function of temperature.

The course and character of the TG curves are influenced by several experimental factors, such as the rate of heating and the atmosphere of the furnace, the geometry of furnace and sample holder, the speed of the recording device, quantity of the sample, particle size, heat of reaction, compactness of the sample,… etc. This method has the disadvantage that in the case of overlapping processes (which are very frequent in thermal investigations) the individual decomposition reactions merge into one another, so that the evaluation of the TG curves becomes difficult.

TG curves are normally plotted with the mass change, Δm, expressed as a percentage on the vertical axis and the temperature, T, or time, t, on the horizontal axis. A schematic representation of a one stage reaction process observed in the scanning mode is shown in Figure 1.1. The reaction is characterized by two temperatures, T_i and T_f, which are called the initial decomposition temperature and the final temperature, respectively (Hatakeyama and Quinn, 1999).

At a linear heating rate, T_f must be greater than T_i, and the difference, T_f - T_i, is called the reaction interval. For an endothermic decomposition reaction, T_i and T_f both increase with increasing heating rate, the effect being greater for T_f than for T_i (Wendlandt, W.W, 1964).

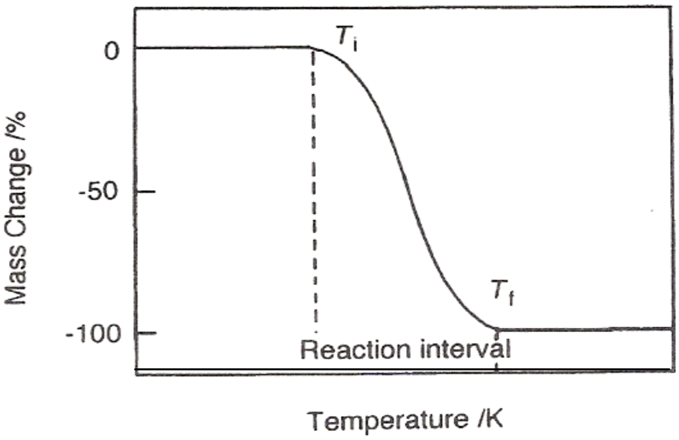


Figure 1.1: Schematic single stage TG curve.

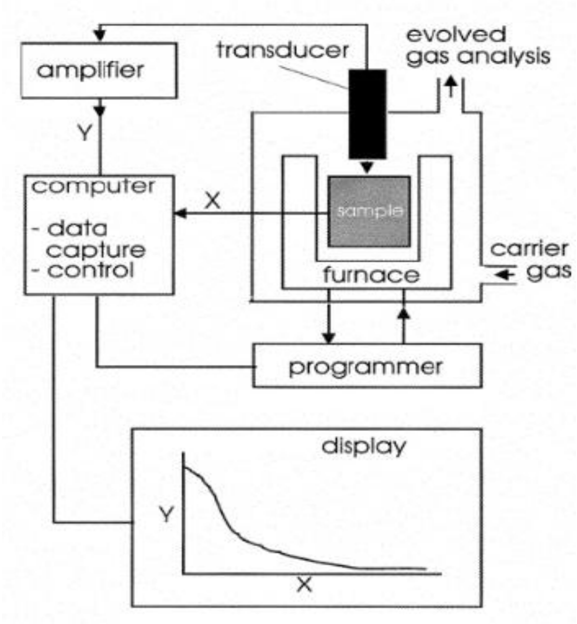


Figure 1.2: A generalized thermal analysis instrument and the resulting thermal analysis curve (Michael E. Brown, 2001).

1.1.2 Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the most widely used of all the thermal analysis techniques. The concept underlying the techniques is simple enough: to obtain information on thermal changes in a sample by heating or cooling it alongside an inert reference.

Historically the techniques have their origin in the measurement of temperature. Figure 1.3 is a schematic representation of the main parts of an instrument. The sample and reference are contained in the DTA/DSC cell. Temperature sensors and the means of heating the sample and reference are incorporated in the cell. Other terms which have been used to describe this part of the instrument include “specimen holder assembly” and more recently “instrument test chamber”. A single computer unit operates the various control functions, data capture and analysis.

The term “differential” emphasizes an important feature of the techniques: two identical measuring sensors are used, one for the sample and one for the reference, and the signal from the instrument depends on the difference between the response of the two sensors. In this way the signal represents the thermal change to be studied free from diverse thermal effects which influence both sensors equally. This has the considerable merit of allowing high sensitivities to be designed into instruments (P.J. Haines, 2002).

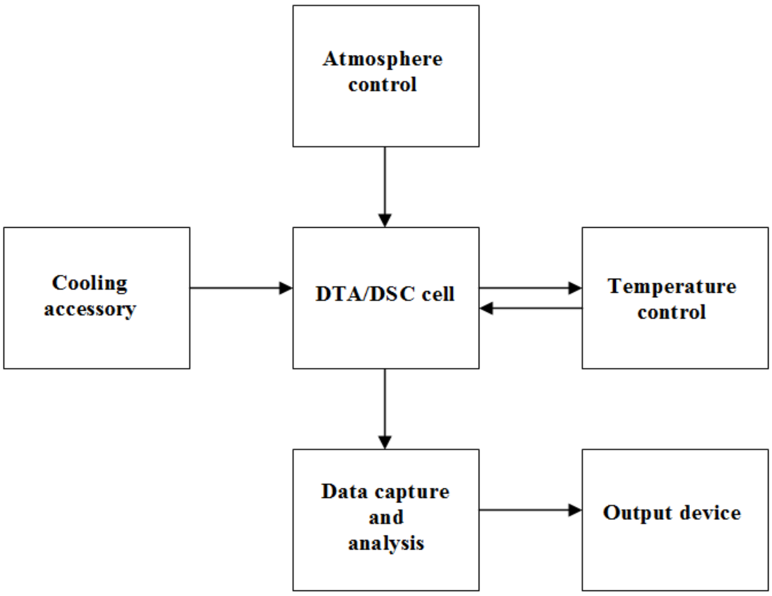


Figure 1.3: Schematic representation of a DTA or DSC instrument (P.J. Haines, 2002).

It is the link with thermal energy which is responsible for the wide ranging applicability of both DTA and DSC. Unlike thermogravimetry the techniques are not dependent on the sample undergoing a change in mass.

DSC is the more recent technique and was developed for quantitative calorimetric measurements. DTA does not lend itself to such measurements and has progressively been replaced by DSC even for measurements in the range 750-1600°C, which at one time were the sole province of DTA. DTA still finds application in the measurement of characteristic temperatures and in the qualitative identification of materials. It remains the technique for measurements above 1600°C where the high temperatures impose considerable design constraints on equipment.

The techniques are most readily applied to the study of solids and whilst their application to liquids is not uncommon more careful attention to experimental practice is required. The small size of samples, often only a few miligrams, and the rapidity with which experiments can be carried out have played an important part in establishing the popularity of the techniques.

The practical distinction between DTA and DSC is in the nature of the signal obtained from the equipment. In the case of a differential thermal analyser it is proportional to the temperature difference,

$$\Delta T = T_s - T_r$$

established between the sample and an inert reference when both are subjected to the same temperature program. The subscripts s and r indicate the sample and reference respectively. The signal from a differential scanning calorimeter will be regarded as proportional to the difference in thermal power between the sample and reference, $d\Delta q/dt$.

The classical temperature programme is a linear temperature change with respect to time. Complex programmes can be implemented by combining different heating or cooling rates with isothermal periods. An example is stepwise heating which may be used to detect the onset of melting under quasi-isothermal conditions. An important innovation has been to overlay the linear temperature change with a regular modulation.

This technique has become known as modulated temperature DSC (MTDSC), or occasionally as temperature modulated DSC (TMDSC).

Most differential scanning calorimeters fall into one of two categories depending on their operating principle: power compensation or heat flux.

Power-compensation: Figure 1.4 (a) shows the main features of the DSC cell - the provision of separate temperature sensors and heaters for the sample and reference.

In the event of a temperature difference arising between the sample and reference, differential thermal power is supplied to the heaters to eliminate the difference and to maintain the temperature at the program value. The differential thermal power is the source of the instrument signal.

Heat flux: In this case the instrument signal is derived from the temperature difference established when the sample and reference are heated in the same furnace. The temperature difference is measured by the temperature sensors-usually thermocouples arranged back-to-back.

Figure 1.4 (b) shows the arrangement of the thermocouples and the single furnace. The difference between heat flux DSC and DTA lies in the conversion of ΔT into differential power. The algorithm for this conversion is contained in the instrument software. The design of the DSC cell is critical if the algorithm is to be transferable from one experiment to another, independent of the sample. The heat flux approach is a development of older forms of “quantitative” DTA.

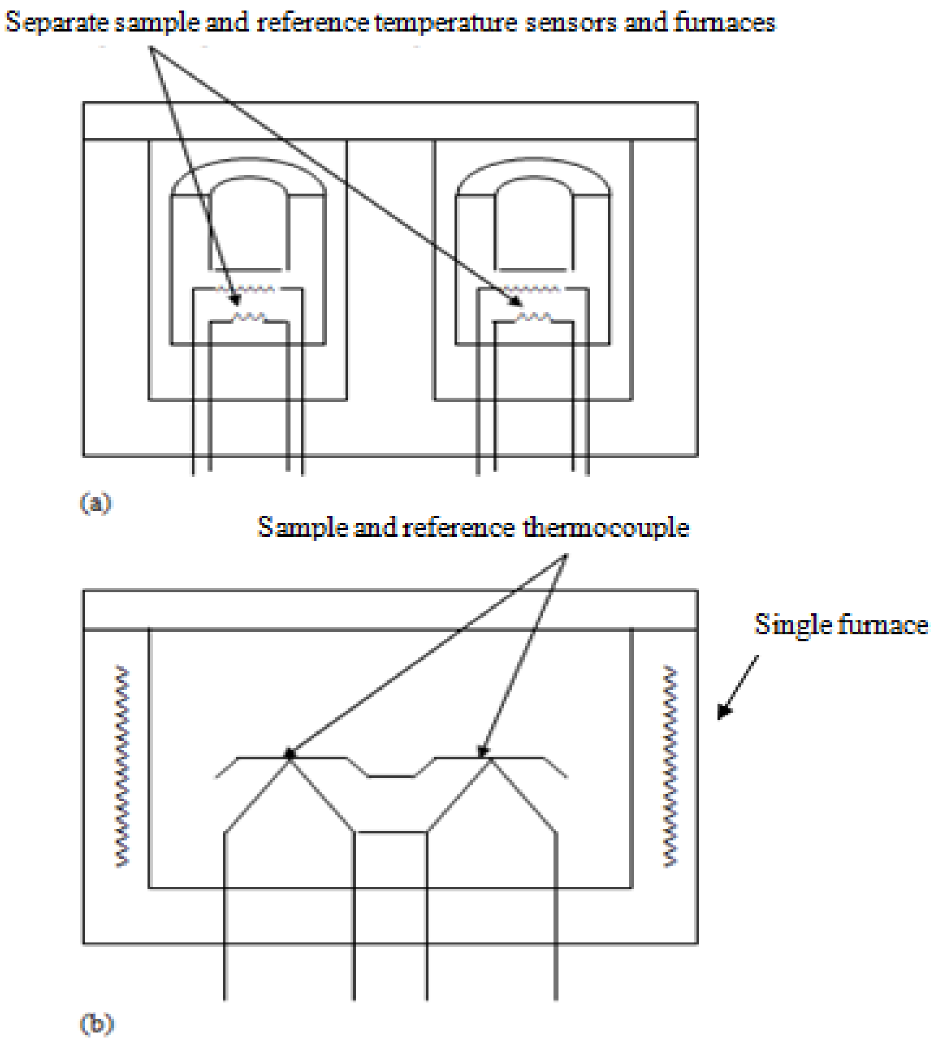


Figure 1.4: (a) Power-compensation differential scanning calorimeter (b) Heat flux differential scanning calorimeter (P.J. Haines, 2002).

Both types of differential scanning calorimeters make use of a crucible to contain the sample. The reference is either an inert material in a crucible of the same type as that used for the sample or simply the empty crucible. Crucibles commonly measure 5-6 mm in diameter, which gives some idea of the overall dimensions of the DSC cell.

It is the provision of dynamic conditions in which the sample is subjected to a controlled heating or cooling program which sets DSC apart from other calorimetric techniques and is a key factor in its wide range of different applications.

Most differential scanning calorimeters are of the heat flux type. Recently a differential scanning calorimeter has been designed which incorporates features of both power compensation and heat flux instruments.

The results from DTA and DSC experiments are displayed as a thermal analysis curve in which the instrument signal is plotted against temperature - usually the sample temperature - or time.

Figure 1.5 shows some of the terminology relating to the results from DSC experiments. The description “heat flow” is frequently used for the instrument signal.

Of particular importance is the extrapolated onset temperature T, which is defined as the temperature of intersection between the extrapolated initial base line and the tangent or line through the linear section of the leading edge of the peak. This temperature rather than the peak maximum temperature T, is frequently used to characterise peaks because it is much less affected by the heating rate.

The temperatures T_i and T_f are the initial and final temperatures of the peak which are sometimes more difficult to pin-point precisely. The terms “isothermal” and “dynamic” refer to the operating mode of the instrument. In the figure the peak represents an exothermic event (exotherm) and has been represented as a positive displacement.

This is the usual convention for DTA and heat flux DSC. In the case of power-compensation DSC exotherms are negative displacements. Where confusion is likely to arise the direction of the exotherms/endotherms should be shown on the thermal analysis curve.

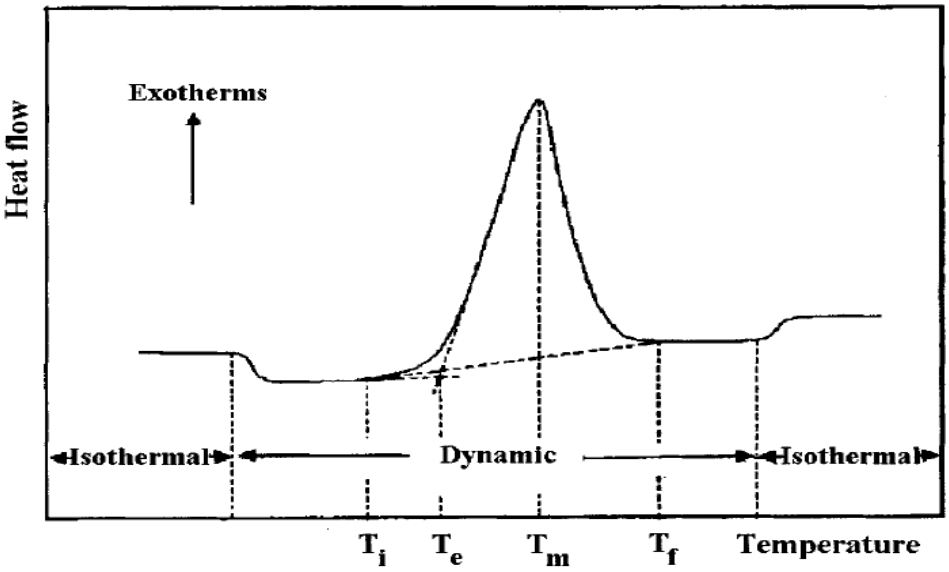


Figure 1.5: Schematic representation of thermal analysis curve (P.J. Haines, 2002).

The alternative format for the thermal analysis curve is the plot of the instrument signal against time. The quantitative advantage of DSC over DTA lies in the relationship between the area enclosed by peaks measured in this format and the corresponding heat change: unlike DTA, with DSC the proportionality is independent of the heat capacity of the sample.

1.1.2.1 Applications of DTA and DSC

The versatility of DTA and DSC can be seen in both the range of materials studied and the type of information obtained. From the standpoint of materials studied the techniques may be regarded as virtually universal in their applicability. Some idea of the range is given in Table 1.3.

Although DSC is a quantitative technique it finds application alongside DTA as a qualitative tool whereby the thermal analysis curve is used as a fingerprint for identifying substances.

The techniques may form part of a quality control procedure in which the presence or absence of a peak in the thermal analysis curve is all that is relevant.

The identification of polymorphs in the context of pharmaceuticals is particularly relevant since different species may have quite different physiological actions.

The investigation of potential reactivity between components of drugs as revealed by changes in the thermal analysis curve represents another significant application of these techniques.

DTA and DSC have found valuable application in the study of phase diagrams both in pharmaceuticals and more widely in the general area of material science.

The materials studied by DTA and DSC:

- Polymers, glasses and ceramics,
- Oils, fats and waxes,
- Clays and minerals,
- Coal, lignite and wood,
- Liquid crystals,
- Explosives, propellants and pyrotechnics,
- Pharmaceuticals,
- Biological materials,
- Metals and alloys,
- Natural products,
- Catalysts.

The greatest impact of the techniques has been seen in the study of polymeric materials with crystallinity and melting behaviour, glass transitions, curing processes and polymerisation representing the different types of thermal behaviour under investigation.

A measure of the importance of this area of activity is reflected in the considerable number of publications and conference presentations it has generated (P. J. Haines, 2002).

1.2 Kinetics of Thermal Degradation

Generally, the thermal degradation of a polymeric material follows more than one mechanism. The existence of more than one concurrent chemical reaction accompanied by other physical phenomena such as evaporation and ablation introduce further complications for the modelling of degradation kinetics.

The development of workable models able to describe the degradation kinetics of polymers has been the concern of many authors. Kinetic study of thermal degradation provides useful information for the optimisation of the successive treatment of polymer materials in order to avoid or at least limit thermal degradation.

The analysis of the degradation process becomes more and more important due to an increase in the range of temperatures for engineering applications, recycling of post-consumer plastic waste, as well as the use of polymers as biological implants and matrices for drug delivery, where depolymerisation is an inevitable process affecting the lifetime of an article.

Additionally, scission of macromolecules driven by thermal fluctuations at elevated temperatures provides a good example for the analysis of population dynamics in complex systems. This subject has therefore attracted substantial attention recently.

A valuable approach for measuring thermal degradation kinetic parameters is controlled transformation-rate thermal analysis (CRTA) – a stepwise isothermal analysis and quasi-isothermal and quasi-isobaric method. In this method, some parameters follow a predetermined programme as functions of time, this being achieved by adjusting the sample temperature.

This technique maintains a constant reaction rate, and controls the pressure of the evolved species in the reaction environment. CRTA is, therefore, characterised by the fact that it does not require the predetermined temperature programmes that are indispensable for TG.

This method eliminates the underestimation and/or overestimation of kinetic effects, which may result from an incomplete understanding of the kinetics of the solid-state reactions normally associated with non-isothermal methods. (K. Pielichowski and James Njuguna, 2005)

1.3 Accuracy of Mathematical Evaluation of Curves

The two basic approaches to determining reaction rate kinetic parameters are isothermal methods and non-isothermal (dynamic) methods.

Non-isothermal analysis is generally preferred for the following reasons: (i) dynamic experiments are quicker and the results widely considered easier to interpret; (ii) the reaction process can be followed over a wide temperature range; (iii) several reaction steps can be observed in a single experiment; and (iv) a number of methods of data evaluation are available.

It is commonly believed that a single dynamic curve is equivalent to a large number of comparable isothermal curves and the theories developed for estimating isothermal reaction rate kinetic parameters can be applied to non-isothermal data (Hatakeyama and Quinn, 1999).

The shape of the thermogravimetric curve is a function of the reaction kinetics and can be used to evaluate kinetic parameters of reactions involving weight changes of the four following types.

$A_s \rightarrow B_s + C_g$
$A_s + B_g \rightarrow C_s$
$A_s + B_s \rightarrow C_s + D_g$
$A_s \rightarrow A_g$

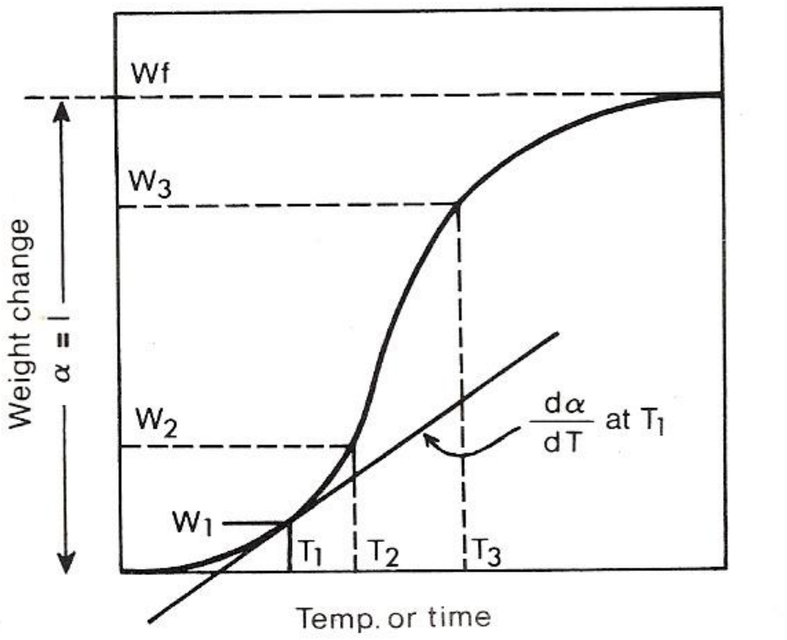


Figure 1.6: Kinetic data from TG experiments at T_2, $\alpha=W_2/W_f$; at T_3, $\alpha=W_3/W_f$.

In TG experiments the data collected is weight loss against temperature or time. This is converted to weight change and then fraction decomposed against time. The value dα/dt which is called the rate of the decomposition reaction is the tangent to the line at any T value. Figure 1.6 shows this point.

The following general equation is used to describe kinetics of thermally induced reactions in the solid state.

$$\frac{d\alpha}{dt} = k\,f(\alpha) \qquad (1.1)$$

where α is the degree of conversion, t is the time, k is the rate constant and f(α) is a function called the reaction model (Singh, et al., 2004). The fraction of starting material consumed, α is given by

$$\alpha = \frac{(W_0 - W)}{(W_0 - W_f)} \qquad (1.2)$$

where W_0, W and W_f are the initial, actual and final mass of the sample, respectively.

In Eq. 1.1 the term of k, the temperature dependence of the rate constant, is expressed by the Arrhenius equation

$$k = Ae^{-E/RT} \tag{1.3}$$

where A (1/s) is the pre-exponantial factor, E (kJ/mol) is the activation energy, R (J/mol. K) is the gas law constant and T (K) is the temperature of the sample. This equation can be substituted into the Eq. 1.1 to give

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \tag{1.4}$$

For reactions in the gas phase and solution, i.e. homogeneous reactions, the equation

$$-\frac{dC}{dt} = kC^n \tag{1.5}$$

where C is the concentration. It might be held that since the equivalent expression in solid state decomposition is

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1.6}$$

then

$$f(\alpha) = (1 - \alpha)^n \tag{1.7}$$

where n is the reaction order. For the rate of solid state decomposition reactions, the equation

$$\frac{d\alpha}{dt} = Ae^{-E/RT}(1-\alpha)^n \tag{1.8}$$

When the temperature of the sample is increased at a constant heating rate, q, the temperature at any time, t, is

$$T = T_0 + qdt \tag{1.9}$$

where T_0 is starting temperature. Differentiating and rewriting this equation we obtain

$$q = \frac{dT}{dt} \tag{1.10}$$

By substitution of Eq. 1.10 into Eq. 1.8 the following equation can be written

$$\frac{d\alpha}{dt} = q\frac{d\alpha}{dT} = Ae^{-E/RT}(1-\alpha)^n \tag{1.11}$$

Integrating and rewriting this equation we obtain

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{q}\int_{T_0}^{T} e^{-E/RT}dT \tag{1.12}$$

or

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{AE}{qR}p(x) = \Phi \tag{1.13}$$

where Φ is the integration of temperature and x=-E/RT. And p(x) is written as

$$p(x) = -\frac{e^x}{x} + \int_{-\infty}^{x} \frac{e^{-x}}{x}dx \tag{1.14}$$

By integrating the left-hand side of Eq. 1.13 the following equations are written as

$$\frac{(1-\alpha)^{1-n} - 1}{(1-n)} = \frac{AE}{qR}p(x) \qquad (n\neq 1) \tag{1.15}$$

$$\ln(1-\alpha) = \frac{AE}{qR}p(x) \qquad (n=1) \tag{1.16}$$

There are various expansions for the term of p(x):

The right-hand side of Eq. 1.11 can not be integrated and an abundance of methods for estimating non-isothermal kinetic parameters deal with this problem so that values of A, E and n can be calculated from a single curve or from a series of curves recorded at different heating rates. The schemes for dealing with Eq. 1.11 are normally classified in four groups. This classification was proposed by Flynn and Wall (1966):

1)Integral methods such as Ozawa's, Coats and Redfern's, Horowitz and Metzger's, Flynn and Wall's method's,

2)Differential methods such as van Krevelen's, Kissinger's, Friedman's methods,

3)Difference-differential methods such as Freeman-Carroll's, MacCallum-Tanner's methods.

4)The methods using for initial reaction rate,

5) Non-linear heating rate methods.

With isothermal methods one assumes several mechanisms and by substitution of experimental data one determines the most convenient one. However, this procedure is much more complicated when the method of rising temperature is used and, therefore, the evaluation of thermogravimetric curves will be founded on the formal kinetic equation.

1.4 Integral Methods

Doyle (1961) introduced a procedure for deriving kinetic data from a TG curve based on the assumption that a single non-isothermal TG curve is equivalent to a large number of comparable isothermal curves. At a constant heating rate q, substituting the Arrhenius equation for k and integrating, Eq. 1.1 becomes

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = -\frac{A}{q} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \qquad (1.17)$$

The function,

$$p\left(\frac{E}{RT}\right)=\frac{R}{E}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)dT \tag{1.18}$$

is introduced and values of p(E/RT) are calculated for the normal range of experimental values $10 \leq E/RT \leq 30$. When $E/RT \geq 20$ a linear approximation is made:

$$\log p\left(\frac{E}{RT}\right)\approx -2{,}315-0{,}4567\left(\frac{E}{RT}\right) \tag{1.19}$$

This method was further simplified by Ozawa (1965). Ozawa method is more widely applicable than the others. Ozawa considered the effect of heating rate and it was shown that a master curve might be derived from the data at different heating rates. For a given fractional mass the left-hand side of Eq. 1.17 is constant and therefore

$$\left(\frac{AE}{q_1R}\right)p\left(\frac{E}{RT_1}\right)=\left(\frac{AE}{q_2R}\right)p\left(\frac{E}{RT_2}\right)=.... \tag{1.20}$$

Substituting Doyle’s approximation (1961):

$$-\log q_1-0{,}4567\left(\frac{E}{RT_1}\right)=-\log q_2-0{,}4567\left(\frac{E}{RT_2}\right)=... \tag{1.21}$$

Eq. 1.21 shows the linear variation of log q with the reciprocal absolute temperature, the slope of the straight line being

$$m = -0{,}4567\ E/R \tag{1.22}$$

That is why Ozawa suggests a plot of logq versus 1/T and the determination of m from the equation of the obtained straight line

$$\log q = m\frac{1}{T}+b \tag{1.23}$$

According to Eq. 1.22, the approximate value of the activation energy will be obtained by means of the relation

$$E = -4{,}349m \qquad (1.24)$$

In order to determine the parameter, A, Ozawa suggested the following procedure. By plotting 1-α versus 1/T a thermogravimetric curve is obtained for each heating rate q. By means of a parallel shift these curves can be superposed and a master thermogravimetric curve is obtained.

This master curve is considered by Ozawa to be better than the individual thermogravimetric curves, offering an elimination of experimental errors. By using this master curve and the earlier determined E value, obtained according to Eq. 1.24, a plot of 1-α versus $\log \frac{E}{qR} p\left(\frac{E}{RT}\right)$ is carried out.

By means of a parallel shift this curve can be superposed with some standard curves, obtained theoretically, by plotting 1-α versus $\log \frac{AE}{qR} p\left(\frac{E}{RT}\right)$. These Standard curves are constructed for various n values. A comparison of the shape of the experimental curve with these standard curves gives the apparent reaction order.

The magnitude of the parallel shift, necessary to superpose the experimental curve with the corresponding standard curve, gives directly the value of log A. A linearized approximation to Eq. 1.17 was proposed by Kassman (1985) to evaluate reaction rate kinetic parameters.

A reference temperature is chosen which is based on the initial and final temperatures of the experiment. A solution of the form $\ln g(\alpha) = \ln R + S\phi(T)$ is proposed, where R and S are constants and $\phi(T)$ has the form

$$\left[\left(\frac{T_r}{T}\right)\exp\left(\frac{1-T_r}{T}\right)\right]^2 \approx 1 \qquad (1.25)$$

T_r is the reference temperature and is given by

$$T_r \approx (T_1T_2)^{1/2}\left[1-\frac{(T_1T_2)^{1/2}}{S}\right] \tag{1.26}$$

where T_1 and T_2 are the initial and final temperatures, respectively. From a plot of lng(α) against 1/T, A and E can be estimated. For a reaction in which the order is unknown, Coats and Redfern (1964) derived the following expression:

$$\log\left\{\frac{1-(1-\alpha)^n}{T^2(1-n)}\right\} = \log\frac{AR}{qE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2{,}303RT} \tag{1.27}$$

where α is the fraction of the sample decomposed at time t, and q is the heating rate.

A plot of either $\log[1-(1-\alpha)]^{1-n}/T^2(1-n)$ against 1/T, or, where n=1, $\log[-\ln(1-\alpha)]/T^2$ against 1/T, should result in a straight line of slope -E/2,303R for the correct value of n. The quantity log(AR/qE)[1−(2RT/E)] appears to be reasonably constant for most values of E and in the temperature range over which most reactions occur.

1.5 Differential Methods

Most commonly used differential method was derived by Friedman (1965). Taking logarithms of Eq. 1.11 gives

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[q\left(\frac{d\alpha}{dt}\right)\right] = \ln\left[A(1-\alpha)^n\right]-\frac{E}{RT} \tag{1.28}$$

For various heating rates q, dα/dt and T values are determined at a constant α value. And plots of ln(dα/dt) versus 1/T should give straight lines where the slope of each line is equal to -E/R, while the intercept is $\ln[A(1-\alpha)^n]$.

Then according to Eq.1.28 plotting $\ln[A(1-\alpha)^n]$ against ln(1−α) gives a slope from which reaction order n, can be calculated. The intercept should be equal to lnA.

Derivation of Eq. 1.28 for a constant α or dα/dt value the following equations are obtained:

$$\frac{d\ln\frac{d\alpha}{dt}}{d\left(\frac{1}{T}\right)} = -\frac{E}{R} = n\frac{d\ln(1-\alpha)}{d\left(\frac{1}{T}\right)} \quad (\alpha\text{=constant}),\ (d\alpha/dt\text{=constant}) \tag{1.29}$$

$$\frac{d\ln\frac{d\alpha}{dt}}{d\ln(1-\alpha)} = n \quad (T\text{=constant}) \tag{1.30}$$

Kissinger (1957) proposed an approximation by differentiating Eq. 1.6.

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt}\left(\frac{Eq}{RT^2} - An(1-\alpha)^{n-1}e^{-E/RT}\right) \tag{1.31}$$

The maximum rate occurs at a temperature T_m defined by setting Eq.1.31 equal to zero.

$$\frac{Eq}{RT_{max}{}^2} = An(1-\alpha)^{n-1}e^{-E/RT_{max}} \tag{1.32}$$

Eq. 1.31 can be integrated, assuming a constant heating rate, to obtain the extent of reaction as a function of temperature. The resulting integral is an exponential integral and a simple expression can not be obtained. A satisfactory approximation was obtained by Murray and White (1955) by successive integration by parts.

Using Murray and White's expression, integration of Eq. 1.8 results in

$$\frac{1}{n-1}\left(\frac{1}{(1-\alpha)^{n-1}} - 1\right) = \frac{ART^2}{Eq}e^{-E/RT}\left(1-\frac{2RT}{E}\right) \tag{1.33}$$

At a temperature T_m defined by Eq. 1.32, the value of $(1\text{-}\alpha)_{max}$ is given by Eq. 1.33.

If Eq. 1.32 is combined with Eq. 1.33, the following results obtained, applicable for n not equal to zero or unity.

$$\frac{1}{n-1}\left(\frac{1}{(1-\alpha)_{max}{}^{n-1}}-1\right)=\frac{1}{n}\frac{1}{(1-\alpha)_{max}{}^{n-1}}\left(1-\frac{2RT_{max}}{E}\right) \qquad (1.34)$$

which simplifies to

$$n(1-\alpha)_{max}{}^{n-1}=1+(n-1)\frac{2RT_{max}}{E} \qquad (1.35)$$

Eq. 1.35 does not contain the heating rate q except as T_m varies with heating rate. The product $n(1\text{-}\alpha)_{max}{}^{n-1}$ is not only independent of q, but is very nearly equal to unity.

Substituting this value in Eq. 1.32 and differentiating, neglecting small quantities, then

$$\frac{d\left(\ln\frac{q}{T_{max}{}^{2}}\right)}{d\left(\frac{1}{T}\right)}=-\frac{E}{R} \qquad (1.36)$$

regardless of reaction order. Eq. 1.36 makes possible the determination of the activation energy, E, for a simple decomposition reaction regardless of reaction order.

1.6 Difference-Differential Methods

A method that is widely employed to calculate rate parameters is that of Freeman and Carroll (1958), where Eq. 1.8 is rewritten in logarithmic form as follows:

$$\log\left(\frac{d\alpha}{dt}\right)=n\left[\log(1-\alpha)\right]+\log A-\frac{E}{2{,}303R}\left(\frac{1}{T}\right) \qquad (1.37)$$

Differentiating the above equation with respect to ln(1-α) gives

$$\frac{d\left[\log(d\alpha/dt)\right]}{d\left[\log(1-\alpha)\right]}=n-\frac{E}{2{,}303R}\frac{d(1/T)}{d\left[\log(1-\alpha)\right]} \qquad (1.38)$$

Therefore a plot of

$$\frac{d[\log(d\alpha/dt)]}{d[\log(1-\alpha)]} \text{ versus } \frac{d(1/T)}{d[\log(1-\alpha)]} \tag{1.39}$$

results in a straight line of slope -E/(2,303R) and intercept n. The order of reaction and the activation energy are calculated from a single experimental curve.

A problem in calculating n by this method is that because the slope of the best-fit line to the data points has a very large absolute value, a small error in the estimation of the slope results in considerable uncertainty in the value of n.

As a result, it is often impossible to distinguish with confidence between the various proposed reactions mechanisms using this procedure.

1.7. Non-isothermal methods

Non-isothermal methods are used for solid state reaction mechanism and kinetic studies. Most of the methods base on Arrhenius equation

$$k=A\exp(-E_a/RT) \tag{1.40}$$

and rate expression,

$$\frac{d\alpha}{dt}=kf(\alpha) \tag{1.41}$$

In equation 1.41, f(x) is a function dependence on reaction mechanism and α is degradation fraction in the range of 0-1 at solid reactants during reaction. If $f(\alpha)=(1-\alpha)^n$ and $dT/dt=\beta$, equation 1.41 can be written as follows:

$$g(\alpha)=\int_0^{\alpha}[\frac{1}{(1-\alpha)^n}]d\alpha=\frac{A}{\beta}\int_{T_0}^{T}\exp\left(\frac{-E_a}{RT}\right)dT \tag{1.42}$$

In equation 1.42, n is reaction order. Equation 1.43 can be written for n=1, equation 1.44 can be written for n≠0.

$$\int_0^{\alpha}[\frac{1}{(1-\alpha)^n}]d\alpha=-\ln(1-\alpha) \tag{1.43}$$

$$\int_0^{\alpha}[\frac{1}{(1-\alpha)^n}]\,d\alpha = -\frac{1-(1-\alpha)^{1-n}}{1-n} \qquad (1.44)$$

The following methods and their equations are used in this study.

Coats and Redfern method

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{E\beta}(1-\frac{2RT}{E})\right) - \frac{E}{RT} \qquad (1.45)$$

A straight line can be obtained from the line which is drawn between $\ln(g(\alpha)/T^2)$ versus 1000/T. The slope of the line gives –E/R.

Wanjun-Yuwen-Hen-Cunxin method

$$\ln\left[\frac{g(\alpha)}{T^{1.8946}}\right] = \left[\ln\frac{AR}{\beta E} + 3.6350 - 1.8946\ln E\right] - 1.0014\left(\frac{E}{RT}\right) \qquad (1.46)$$

A straight line can be obtained from graphic which is drawn between $\ln(g(\alpha)/T^{1.8946})$ versus 1/T. The slope of the line gives –E/R and also set intercept ordinate gives pre-exponential factor.

Madhusudanan-Krishnan-Ninan method

$$\ln\left[\frac{g(\alpha)}{T^{1.9206}}\right] = \ln\left(\frac{AE}{\beta R}\right) + 3.7678 - 1.9206\ln E - 0.12040\left(\frac{E}{T}\right) \qquad (1.47)$$

The slope of the line drawn between $\ln(g(\alpha)/T^{1.9206})$ versus 1/T gives activation energy and the set intercept ordinate gives pre-exponential factor.

MacCallum-Tanner method

$$-\log g(\alpha) = \log\frac{AE}{\beta R} - 0.4828E^{0.4351} - \frac{449+217E}{T.10^3} \qquad (1.48)$$

The slope of the line drawn between ln g(α) versus 1/T gives activation energy and the set intercept ordinate gives pre-exponential factor.

Horowitz-Metzger method

Horowitz-Metzger defines a characteristic temperature and parameter with equation 1.49.

$$\Theta = T - T_m \tag{1.49}$$

If reaction order equals to 1, a characteristic temperature can be determined at $(1-\alpha)_m = 1/e = 0.368$ and equation 1.50 can be obtained.

$$\ln \ln g(\alpha) = \frac{E\theta}{RT_m^2} \tag{1.50}$$

If reaction order is not known, it can be determined at a characteristic temperature for maximum heating rate. When $\Theta = 0$, $(1-\alpha) = (1-\alpha)_m$ and $(1-\alpha)_m = n^{1/1-n}$, equation 1.51 can be obtained.

$$\ln g(\alpha) = \ln \frac{ART_m^2}{\beta E} - \frac{E}{RT_m} + \frac{E\theta}{RT_m^2} \tag{1.51}$$

Activation energy can be calculated from the line drawn between ln g(α) versus Θ.

van Krevelen method

van Krevelen et al. have found the first theoretical expression from thermogravimetric data. They used an approximation for exponential integral to obtain equation 1.52.

$$\log g(\alpha) = B + (\frac{E}{RT_r} + 1) \log T \tag{1.52}$$

where

$$B = \frac{A}{\beta}(\frac{E}{RT_r} + 1)^{-1}(\frac{0.386}{Tr})^{E/RT_r}$$

T_r is the reference temperature. The slope of line drawn between log g(α) versus logT gives activation energy.

Tang method

Using a suitable approximation to solve equation 1.41, when it is taken logarithm each side, equation 1.53 can be obtained.

$$\ln\left(\frac{\beta}{T^{1.894661}}\right)=\ln\left(\frac{AE}{R\,g(\alpha)}\right)+3.635041-1.894661\,\ln E-\frac{1.001450\,E}{R\,T} \qquad (1.53)$$

Activation energy can be obtained from the slope of Arrhenius lines calculated for the same degradation values at different heating rate.

Kissinger-Akahira-Sunose method

Kissinger-Akahira-Sunose (KAS) method is an isoconversional method like two other methods and calculation of activation energy is done like 2 other methods. Equation 1.54 can be obtained according to KAS method.

$$\ln\left[\frac{\beta}{T^2}\right]=\ln\left[\frac{AR}{E\,g(\alpha)}\right]-\frac{E}{RT} \qquad (1.54)$$

The slope of line drawn between $\ln(\beta/T^2)$ versus 1/T gives activation energy.

Kissinger method

Activation energy can be calculated using equation 1.55 with Kissinger method without know the solid state degradation reaction mechanism.

$$\ln(\frac{\beta}{T_{max}^2})=\left\{\ln\frac{AR}{E}+\ln[n(1-\alpha_{max})^{n-1}]\right\}-\frac{E}{RT_{max}} \qquad (1.55)$$

β is heating rate, T_{max} is temperature related to maximum reaction rate, A is pre-exponential factor, α_{max} is maximum degradation fraction, n is reaction order. The slope of line drawn between ln (β/T_{max}^2) versus $1000/T_{max}$ gives activation energy.

Flynn-Wall-Ozawa method

This method is an integral method. Pre-exponential factor (A) and activation energy (E) is not depend on degradation fraction, but they depend on the temperature. This method uses equation 1.56.

$$\log g(\alpha) = \log \frac{AE}{R} - \log \beta + \log p\left(\frac{E}{RT}\right) \tag{1.56}$$

If E/RT>20, Doyle approximation is used and equation 1.57 can be obtained.

$$\log \beta = \log \frac{AE}{R} - \log g(\alpha) - 2.315 - 0.4567 \frac{E}{RT} \tag{1.57}$$

Friedman method

Friedman method uses equation 1.58 for thermal degradation kinetic based on Arrhenius expression.

$$\ln(\frac{d\alpha}{dt}) = \ln(A) + n \ln(1-n) - \frac{E}{RT} \tag{1.58}$$

A is degradation fraction in t time, R is gas constant and T is temperature. The plot of ln(dα/dt) versus 1/T should be linear with the slope E/R, from which E can be obtained.

α, $g(\alpha)$, β, T_m, E, A, and R are respectively degradation fraction, integral function of degradation, heating rate, DTG peak temperature, pre-exponential factor and gas constant in above equations.

1.8 General Information about Polymers

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed monomers, and the reaction by which they combine are termed polymerization. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule.

When one speaks of polymers, one is concerned with materials whose molecular weights may reach into the hundreds of thousands or millions.

There has been and still is considerable confusion concerning the classification of polymers. During the development of polymer science, two types of classifications have come into use.

One classification is based on polymer structure and divides polymers into condensation and addition polymers. The other classification is based on polymerization mechanism and divides polymerizations into step and chain polymerizations.

The condensation–addition classification is based on the composition or structure of polymers. The step–chain classification is based on the mechanisms of the polymerization processes.

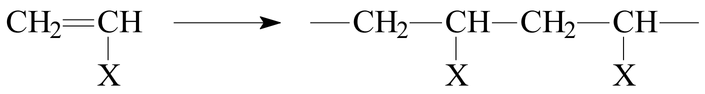
1.9 Syntesis of Polymers

In 1929 W. H. Carothers suggested a classification of polymers into two groups, condensation and addition polymers.

1.9.1 Addition Polymerization

Addition polymers were classified by Carothers as those formed from monomers without the loss of a small molecule. Unlike condensation polymers, the repeating unit of an addition polymer has the same composition as the monomer. The major addition polymers are those formed by polymerization of monomers containing the carbon–carbon double bond.

The most important group of addition polymers includes those derived from unsaturated vinyl monomers:



$$\mathrm{CH_2{=}\underset{\overset{|}{X}}{CH}} \longrightarrow \mathrm{-CH_2-\underset{\overset{|}{X}}{CH}-CH_2-\underset{\overset{|}{X}}{CH}-}$$

1.9.2 Condensation Polymerization

Condensation polymers were those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water, ammonia…etc.

Table 1.3: Distinguishing features of addition and condensation polymerization mechanism.

Addition (Chain) Polymerization	Condensation (Step) Polymerization
Only growth reaction adds repeating units one at a time to the chain	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction	Monomer disappears early in reaction: at DP (Degree of Polymerization) 10, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Long reaction times give high yields but affect molecular weight little.	Long reaction times are essential to obtain high molecular weights.
Reaction mixture contains only monomer, high polymer, and about 10^{-8} part of growing chains.	At any stage all molecular species are present in a calculable distribution.

1.9.3 Oxidative Polymerization

Oxidative polymerization reactions are similar to condensation polymerizations and addition polymerizations although they have different properties than those polymerizations. Basic properties of these reactions are given as follows;

1. Oxidative polymerization reactions occur by main aromatic compounds.

2. There is the necessity of the use of oxidant in oxidative polymerization reactions.

3. These reactions are similar to condensation reactions. Because small molecules like H_2O, HCl leave the structure at the end of the reactions.

4. Side groups which give electrons increase the activity of monomer and the yield of polymer in oxidative polymerization reactions.

5. Oxidative polymerization reactions are irreversible. The polymer chains formed, do not interact with the polymers with functional groups and the materials with small molecule.

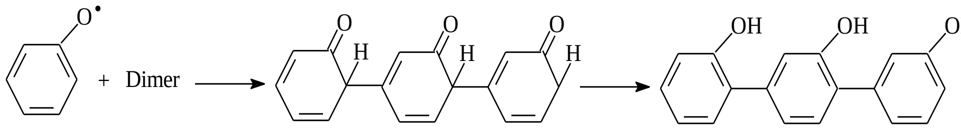
6. There is always monomer in media during the progression of the polymerization.

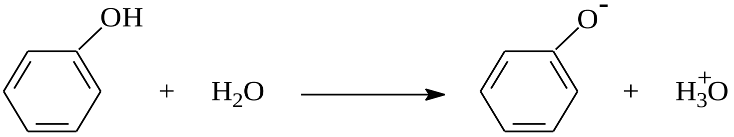
Apparently, oxidative polymerization reactions with its some properties are similar to condensation reactions and with its some properties are similar to addition reactions. Therefore, these reactions are called as oxidative polycondensation or oxidative polymerization in some scientific sources.

1.9.3.1 Oxidative Polymerization of Phenols

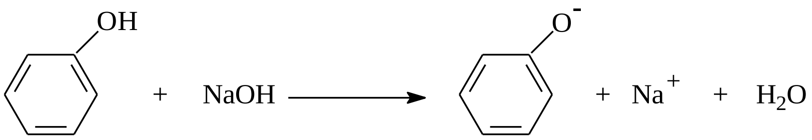
Phenolic aromatic compounds undergo oxidative polymerization easier than aromatic hydrocarbons against oxidants, because of the fact that they have functional groups in their structure. As known, O-H bond has less energy than C-H bond does and the polarity of O-H bond is higher than that of C-H bond. Therefore, homolytic decomposition of O-H bond in phenols with the effect of oxidants, occurs very easily.

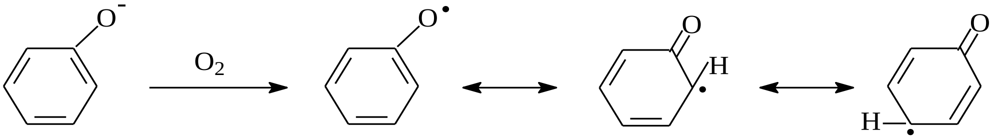
Phenols, like water, ionize in polar solvent with the effect of molecules of the solvent.





Ionization takes place better in basic media and phenolate anions are formed.



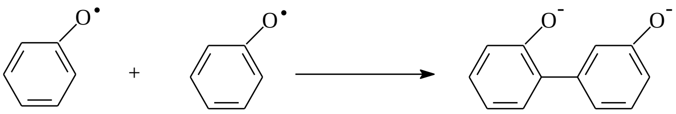


I II III

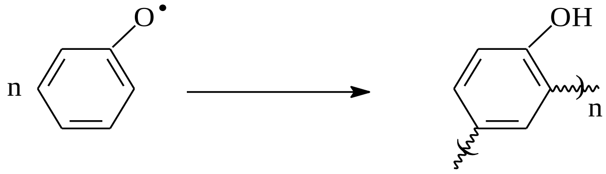
Phenolate anions transform to phenoxy radicals rapidly and easily in the presence of the oxidant, in oxidative polycondensation polymerization.

The phenoxy radicals are very active and unstable molecules which form diphenol structure combining rapidly with each other.

At the following stage, diphenolates transform to phenol-phenoxy radicals again with the effect of oxidants in the media, and this new radicals form trimer and tetramer combining with each other as it is shown for trimer example as follows:



At the next stages –di, -tri, -tetra and polymers form as shown belove:



Nowadays various polyphenols are being synthesized using phenols and derivatives such as phenol, cresol, α and β naphtols, hydroquinone and resorcinol…etc. by the method of oxidative polymerizaiton. It is reported that in the literature that the probability of occurrence oxidative polycondensation increase with ascend of number of OH group in aromatic alcohols and number of aromatic ring as follows:

phenol < p-cresol < α-naphtol < β-naphtol < catechol < resorcinol < hydroquinone

Because of the fact that the dioxy compounds derived from these molecules have very high activity as they react with H_2O_2 and NaOCl very rapidly at room temperature releasing heat, and so they react to give an oxidative polycondensation reaction. On the other hand it is necessary to heat the other phenol derivatives to react for polycondensation. Phenols have a high reactivity so, unlike the hydrocarbons, there is no need the catalyst in polymerization.

H_2O_2, NaOCl and oxygen are used as oxidant in the oxidative polycondensation of phenols. There are many advantages of these oxidants in practise. They are widely-used, so cheap and useful in terms of technology.

The most active oxidant is NaOCl which is used for oxidative polycondensation of phenols having low activity. NaCl is released as by product when NaOCl is used. This salt is possibly used for other purposes after purification.

There are advantages of H_2O_2 oxidant as it transforms to water without forming any by product. On the other hand, H_2O_2 provides that the phenols react to yield oxidative polycondensation at low temperatures (20-50°C) in the presence of little amount of some catalysts (1-2%). H_2O_2 is much more expensive compared to the other oxidants.

The air oxygen is the most suitable oxidant for oxidative polycondensation reaction since it is very cheap and abundant. Moreover it forms only water during the reaction as by product which is the most important advantage of oxygen. Since the air oxygen is a mild oxidant, it is not utilizable for polymerization of the phenols.

Aromatic and aliphatic solvents are used in oxidative polycondensation of aromatic hydrocarbons. These reactions are carried out in apolar organic solvents because they interact with polar ones.

Oxidative polymerization of phenol is carried out without catalyst in polar solvents such as water, tetrahydrofuran, alcohol, aceticacid,…,etc. From this point of view, the most important solvent is water because it is cheap and safe, and removed readily.

There are two kind of coupling in oxidative polymerization of phenol derivatives. These are C-C and C-O-C couplings. This couplings can take place during polymerization. Kobayashi and Higashimura (2003) have studied on coupling selectivity.

The reaction mechanism of the selectivity for C–O coupling, however, has not been made thoroughly clear yet. First, the following three reaction mechanisms so far proposed are discussed; (i) coupling of the free phenoxy radicals, (ii) coupling of the phenoxy radicals coordinated to catalyst complexes, and (iii) coupling through the phenoxonium cation.

Next, an oxidoreductase enzyme such as peroxidase or oxidase and a peroxidase model complex that have been recently found as the catalyst for oxidative polymerization of phenols are described.

For example, the oxidation of 2,6-dimethylphenol (2,6-Me_2P) by use of benzoyl peroxide or alkaline ferricyanide as oxidant mainly gave 3,3′,5,5′-tetramethyldiphenoquinone (DPQ).

In 1959, Hay and co-workers discovered an oxidative polymerization of 2,6-Me_2P catalyzed by CuCl/pyridine (Py) under dioxygen leading to poly(2,6-dimethyl-1,4- phenylene oxide) (P-2,6-Me_2P).

This is the first example for oxidative polymerization to synthesize a phenolic polymer with high molecular weight (Shiro Kobayashi, Hideyuki Higashimura, 2003).

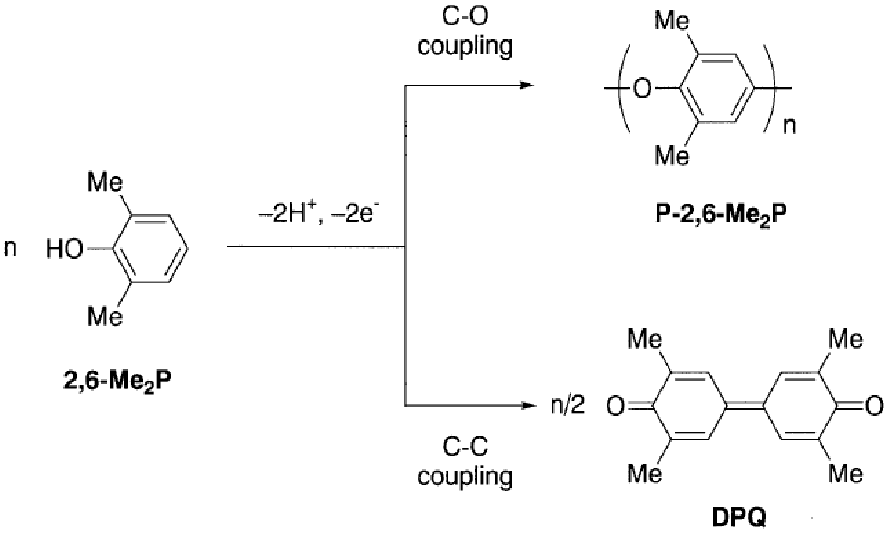


Figure 1.7: Oxidative polymerization of 2,6-Me_2P (Shiro Kobayashi, Hideyuki Higashimura, 2003).

1.10 Applications of Polyphenols

Nowadays there are considerably lots of investigations that have done about schiff based polymers which contain active hydroxyl group (-OH). This kind of polymers have some useful properties like paramagnetism, semi-conductivity, stability in the effect of high energy.

Because of these properties, they are used in preparing composites that have done high stability at high temperature, thermostabilizer, graphite materials, epoxy oligomer and block copolymer, photoresist and in preparing antistatic and flame resistant materials.

These polymers can gain new and useful properties adding different functional groups in their structure. Polyphenols that have various functional groups can be used for cleaning process of toxic heavy metals in industrial waste water. For this reason, the synthesis of polymer-metal complex is very important for analytic and environmental chemistry. Considering these advantages, polymer structured ligands have been prepared and complex forms have been tried with many of transition metals. Thus polyphenols have a wide usage area.

1.11 The Aim of The Study

Determination of relationship between activation energy and molar mass distributions of polymers synthesized were purposed in this study. For this purpose, all the polymers were firstly synthesized by using different poor oxidants such as NaOCl, H_2O_2 and air, and characterized with UV-vis, FT-IR, ^{1}H-NMR and ^{13}C-NMR analysis methods. Then molar mass distributions of polymers were determined by SEC analysis.

Finally, A PC programme design individually by previous researchers was used to calculate the kinetic parameters (F. Doğan, 2006). Kinetic parameters related to the solid state decomposition were determined by using single heating rate and multiple heating rate methods. The influence of molar mass distributions on the activation energy values related to the decomposition of polymers were compared by SEC analysis. As a result kinetic studies, most suitable kinetic method was determined for each polymer.

2 EXPERIMENTAL

2.1 MATERIALS

2.1.1 Chemicals

4- methyl catechol used in synthesis of poly(4-methyl) catechol was supplied by Fluka.

Potassium hydroxide supplied by Merck, Sodium hypochloride (30% aqueous solution) supplied by Paksoy and Hydrogen peroxide (30% aqueous solution) supplied by Merck were used in polymerization processes.

Air oxygen was used as oxidant in polymerization processes.

Hydrochloric acid supplied by Merck was used in neutralization of synthesized materials.

Acetonitrile supplied by Merck and was used to remove the monomer remained in medium after polymerization.

Ethyl alcohol, acetone, 1,4-dioxane, chloroform, 2-propanol, ethyl acetate, carbon tetrachloride, heptane, tetrahydrofuran supplied by Merck were used to test the solubility of synthesized materials.

2.1.2 Instruments

Perkin-Elmer Lamb 25 UV-Vis spectrophotometer, Perkin Elmer Infrared (FT-IR) Spectrophotometer (4000-550 cm^{-1}), Shimadzu VP-10A Size Exclusion Chromotography (SEC) and Bruker AC FT ^{1}H- and ^{13}C- Nuclear Magnetic Resonance Spectrophotometer (NMR) were used to analyse the synthesized materials. Tetra methyl silane(TMS) and dimethyl sulphoxide (DMSO) were used as internal standard and solvent in NMR measurements, respectively.

Perkin Elmer Diamond System Thermogravimetry (TG) and Differential Thermogravimetry (DTG) were used for thermal analyses of the synthesized materials.

2.2 METHOD

2.2.1 Polymerization of 4-methyl Catechol (MC)

MC monomer was polymerized by means of oxidative polymerization in presence of weak oxidant such as sodiumhypochloride, hydrogeneperoxide and air oxygene. First of all, 1x10^{-3} mole of MC (0.0124 g) was dissolved in 0.1 M KOH solution and the final solution was introduced to a three-necked glass flask stirred with a magnetic stirrer and fitted with a thermometer, a dropping funnel which contains either NaOCl (30%) or H_2O_2 solution and a condenser.

In the experiments carried out in air oxygen, 0.1 M KOH solution was added to the reaction mixture in the flask before air flow to neutralize CO_2 in the air. When the polymerization ended, the reaction mixture was cooled to the room temperature and was neutralized with 0.1 M HCl solution.

The precipitate was filtered and was purified from mineral salts by washing three times with 50 mL portions of hot water. The polymer obtained was dryed in an oven at 110°C.

Oxidative polymerization of some diphenolic compounds like catechol, have been studied by Aktaş N. et al. and Dubey S. et al (Aktaş. N., 1998 and Dubey S., 2003). In this work, we have studied polymerization of MC leading to polymeric structure of 1,4- oxyphenylene since it is a catechol derivative (Fig.2.1). ^{1}H-NMR and ^{13}C-NMR analyses support this case (as it will explain next).

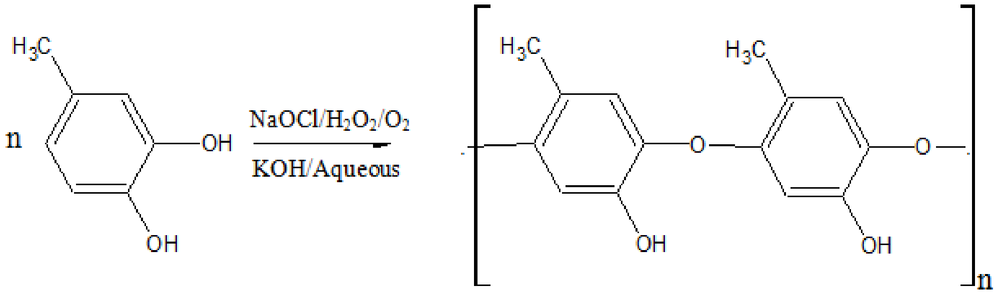


Figure 2.1: Proposed oxidative polycondensation reaction mechanism for PMC.

First phenolate anion of monomer occurs in alkaline and subsequently it transforms to monomeric radicals in presence of the radicalic initiators. 2 different coupling mechanism are possible to form dimer, trimer, tetramer, …, polymer from these radicals as mentioned before. Under the present conditions it is concidered that the monomeric radicals undergo C-O-C coupling during polymerization. The spectroscopic data show that this kind of coupling occurs during the polymerization.

2.2.2 Solubility Determination and Characterization of Polymers

PMC is a powdery polymer with dark brown colour. The solubility test of a polymer was carried out in a test tube at room temperature using 1 mg of the sample and 1 mL of the solvent. As a result PMC, it was seen that PMC dissolved in acetone, tetrahydrofurane (THF), dimethyl phenol (DMP), dimethyl sulfoxide (DMSO), alkaline solvents, concentrated sulphuric acid (H_2SO_4) while it did not dissolve in methanol, ethanol, 1-butanol, iso-propanol, heptane, hexane, benzene, toluene, ethyl-methyl ketone, ethyl acetate, acetonitrile, chloroform, carbon tetrachloride, dioxane.

SEC analysis of polymers was carried out to determine the molar mass distribution i.e. number average molar mass (M_n), weight average molar mass (M_w) and polydispersity index (PDI) of the polymers.

The polymers were characterized by using UV-Visible, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectrophotometric techniques.

TG-DTG thermograms were recorded to calculate the kinetic parameters such as activation energy (E_a),preexponential factor (A) …etc. related to the solid state degradation of the polymers.

3 RESULTS AND DISCUSSION

3.1 Determination of the Conditions for Oxidative Polycondensation of MC

There are considerable investigations carried out about Schiff based polymers with active hydroxyl group (-OH). It is well known that this kind of polymers have some useful properties such as thermal stability, paramagnetism, semi-conductivity, antimicrobial activity. Yet the preparation of this kind of materials using polycondensation reactions, have been started to be investigated just lately. These materials have electro-donor imine group (–C=N–). For this reason, -OH group of these materials is more active than that of phenols in homolytic oxidation reactions. On the other hand, these polymers contain azomethyne group (–HC=N–) linked to phenol in their structure and they undergo change in oxidative polycondensation reactions. So this is an issue of concern. If the azomethyne groups are so stable during this reaction, chemically active schiff base substituted higher polyphenols can be obtained. If the imine bond undergoes oxidative degradation, the polyphenols occured are expected to contain active –CHO and –COOH groups. In both cases, active polyphenols are obtained.

In this study, the conditions of oxidative polycondensation of MC were determined and the solid state degradation kinetics of the polymer was investigated. MC was polymerized in aqeous alkaline solution via phenoxy radicals using NaOCl, H_2O_2 and air oxygen as oxidant at various conditions such as temperature, reaction time and concentration of the initiator. It was observed that the yield of polymerization varied depending on the conditions and type of the oxidants.

3.2 Oxidative Polycondensation of MC with Different Oxidants

3.2.1 Oxidative Polycondensation of MC in presence of NaOCl as oxidant.

The experiments were carried out over a range of temperature 50°C to 90°C with NaOCl depending on time. It was observed that the yield increased upto 80°C while it decreased at 90°C. The reason why is the degradation of the polymer back to monomer. The reaction was run as long as 3 hours to 20 hours. The optimum reaction time was found to be 10 hours. The yield decreased with the decreasing KOH concentration. The highest yield at suitable conditions was found to be 75 percent. The values of yield under different reaction conditions are given in Table 3.1.

Table 3.1: The oxidative polycondensation reaction parameters of polymer with NaOCl.

Sample no	Temperature, ^{0}C	Time, h	[KOH] molL^{-1}	[NaOCl] molL^{-1}	Yield, %
1	50	3	0.024	0.03	21
2	60	3	0.024	0.03	26
3	70	3	0.024	0.03	31
4	80	3	0.024	0.03	35
5	90	3	0.024	0.03	28
6	80	5	0.024	0.03	35
7	80	10	0.024	0.03	61
8	80	15	0.024	0.03	55
9	80	20	0.024	0.03	42
10	80	10	0.024	0.05	63
11	80	10	0.024	0.06	71
12	80	10	0.024	0.12	68
13	80	10	0.024	0.15	66
14	**80**	**10**	**0.018**	**0.06**	**75**
15	80	10	0.015	0.06	60
16	70	10	0.012	0.06	42
17	70	10	0.006	0.06	37

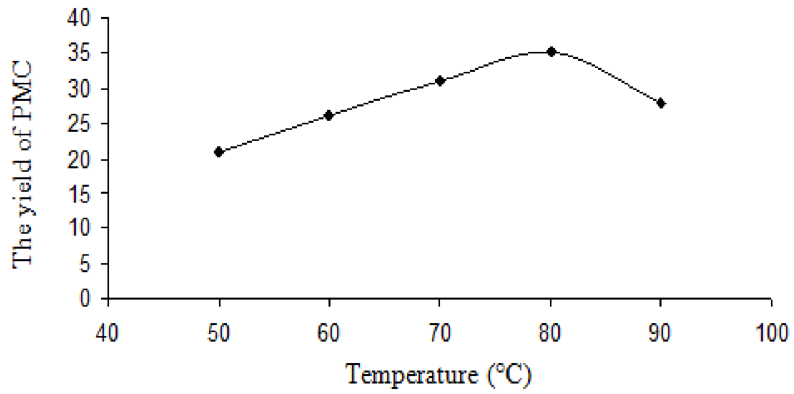


Figure 3.1: Effect of the reaction temperature on the yield of oxidative polycondensation reaction of MC in presence of NaOCl.

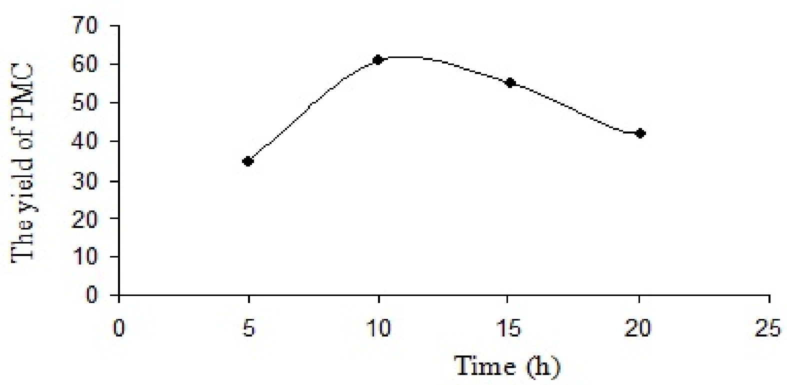


Figure 3.2: Effect of the reaction time on the yield of oxidative polycondensation reaction of MC in presence of NaOCl.

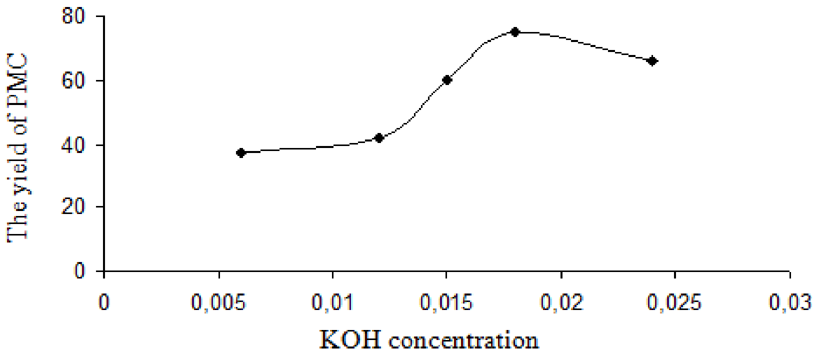


Figure 3.3:.Effect of the KOH concentration on the yield of oxidative polycondensation reaction of MC in presence of NaOCl.

3.2.2 Oxidative Polycondensation of MC in presence of H_2O_2 as oxidant

The oxidative polycondensation of MC was carried out using H_2O_2 as oxidant. The highest yield was obtained at 70°C. It was seen that the yield of polymer decreased above 70°C due to the thermal degradation. The experiments were run for 3 to 20 hours in order to determine the effect of reaction time on the yield. The highest yield which is 44 percent was obtained in the experiment run for 10 hours. The yield decreased with the increasing H_2O_2 concentration.. The yields under different reaction conditions are given in Table 3.2.

Table 3.2: The oxidative polycondensation reaction parameters of polymer with H_2O_2.

Sample no	Temperature, ^{0}C	Time, h	[KOH] $molL^{-1}$	[H_2O_2] $molL^{-1}$	Yield ,%
1	50	3	0.024	0.03	15
2	60	3	0.024	0.03	19
3	70	3	0.024	0.03	21
4	80	3	0.024	0.03	16
5	70	5	0.024	0.03	26
6	**70**	**10**	**0.024**	**0.03**	**44**
7	70	15	0.024	0.03	32
8	70	20	0.024	0.03	31
9	70	10	0.024	0.05	37
10	70	10	0.024	0.06	31
11	70	10	0.018	0.03	21
12	70	10	0.006	0.03	14

3.2.3 Oxidative Polycondensation of MC with Air Oxygen

The experiments were run over a range of temperature 50 to 80°C with air oxygen. It was observed that the yield increased up to 60°C while it decreased above 60°C. The reason why is the degradation of the polymer back to monomer. The reaction time was chosen as 3 to 20 hours. The optimum reaction time was found to be 3 hours. The highest yield was found to be 75 percent. The yields under different conditions are given in Table 3.3.

Table 3.3: The oxidative polycondensation reaction parameters of polymer with air oxygen.

Sample no	Temperature, ^0C	Time, h	[KOH], $molL^{-1}$	Air O_2, L h^{-1}	Yield, %
1	50	3	0.024	8.5	8
2	**60**	**3**	**0.024**	**8.5**	**18**
3	70	3	0.024	8.5	12
4	80	3	0.024	8.5	13
5	60	5	0.024	8.5	11
6	60	10	0.024	8.5	9
7	60	15	0.024	8.5	11
8	60	20	0.024	8.5	12

3.3 SEC Analysis of the Polymers

It was observed in SEC analysis of the polymers that the one obtained in presence of NaOCl (labelled PMC1) formed 3 fractions as those obtained with H_2O_2 (PMC2) and with air oxygen (PMC3) formed 2 fractions (Table 3.4).

For PMC3, low molar mass (M_n: 6100gmol^{-1}; M_w: 6600gmol^{-1}; PDI: 1.081) fraction formed 95 percent of the polymer while higher one (M_n: 23600gmol^{-1}; M_w: 31200gmol^{-1}; PDI: 1.322) did only 5 percent of it. For PMC2, low molar mass (M_n: 7600gmol^{-1}; M_w: 8400gmol^{-1}; PDI: 1.105) fraction formed 95 percent of the polymer while higher one (M_n: 28400gmol^{-1}; M_w: 32400gmol^{-1}; PDI: 1.140) did only 5 percent of it. For PMC1, low molar mass (M_n: 8900gmol^{-1}; M_w: 11600gmol^{-1}; PDI: 1.208) fraction formed 90 percent and low molar mass (M_n: 21000gmol^{-1}; M_w: 29000gmol^{-1}; PDI: 1.380) fraction formed 7 percent of the polymer while higher one (M_n: 59000gmol^{-1}; M_w: 65500gmol^{-1}; PDI: 1.110) did only 3 percent of it.

Table 3.4: Molar mass distribution of the polymers.

		POLYMERS		
		PMC1	PMC2	PMC3
TOTAL	M_n	9600	8800	7100
	M_w	11600	9700	8200
	PDI	1.208	1.102	1.154
FRACTION-1	M_n	8900	7600	6100
	M_w	10500	8400	6600
	PDI	1.171	1.105	1.081
	%	90	95	95
FRACTION-2	M_n	21000	28400	23600
	M_w	29000	32400	31200
	PDI	1.380	1.140	1.322
	%	7	5	5
FRACTION-3	M_n	59000	-	-
	M_w	65500	-	-
	PDI	1.110	-	-
	%	3	-	-

3.4 Structure Analysis of Polymers Synthesized

3.4.1 UV-Vis Spectrum of Polymers

UV-Vis spectral analysis of PMC polymers (PMC1, PMC2, PMC3) was carried out using DMSO at 25°C and spectrum were recorded. The values of peak obtained from spectrum was 287 and 415 nm for PMC1, 285,309 and 425nm for PMC2, 286 and 410 nm for PMC3. The peak value of monomer was 279 and 289 nm.

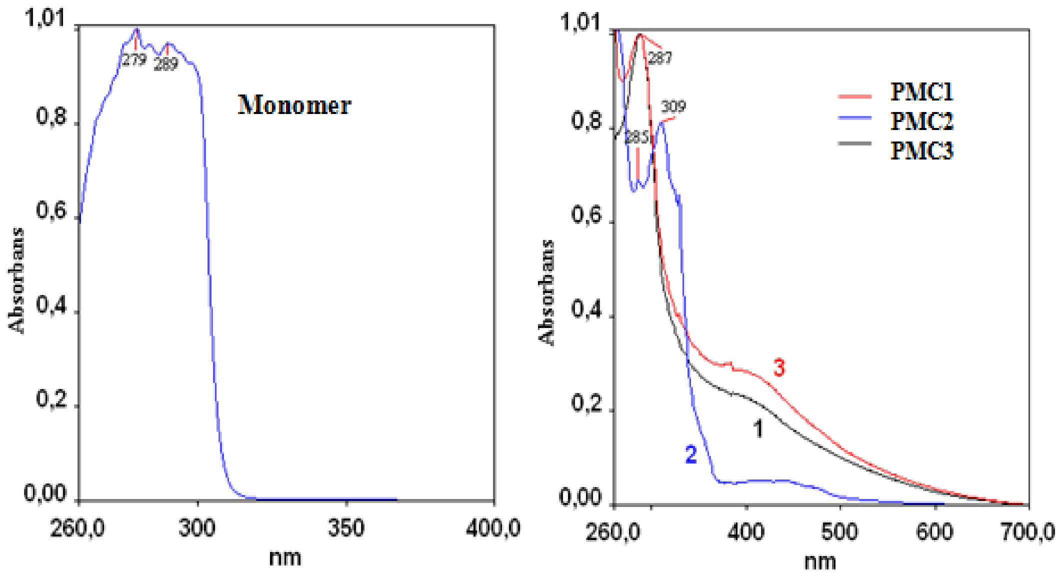


Figure 3.4: Absorption spectrum of MC and PMC.

3.4.2 FT-IR Spectrum of Polymers

FT-IR spectrum of PMC using ATR/FT-IR system are given in Figure 3.5. The absorption wavenumber values related to the spectrum are shown in Table 3.5.

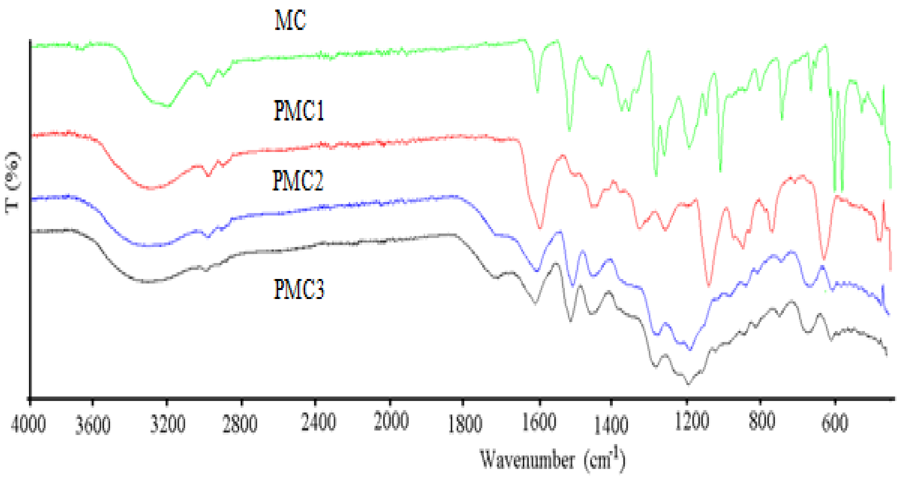


Figure 3.5: FT-IR spectrum of MC and PMC

Table 3.5: The wavenumber values (1/λ) and functional groups of MC and PMC.

	Monomer		Polymer	
Functional group	Stretching vibration	Bending vibration	Stretching vibration	Bending vibration
-OH	3247cm^{-1}	1240 cm^{-1}	3350 cm^{-1}	1242 cm^{-1}
C=C	1602 cm^{-1} 1556 cm^{-1} 1452 cm^{-1}		1610 cm^{-1} 1560 cm^{-1} 1456 cm^{-1}	
Ar-O of phenol ring	1282 cm^{-1}		1286 cm^{-1}	
Aromatic C-H	2947 cm^{-1}		2947 cm^{-1}	
Aliphatic C-H of CH_3	2871 cm^{-1}		2886 cm^{-1}	
C-O-C			1277 cm^{-1}	

There is a significant difference between MC and PMC bands. It is observed in FT-IR spectra of MC and PMC that the bands in the spectrum of the monomer are so sharper than those of the polymers since they have polyconjugate bond structure which absorb IR light over a range of broader wavelength.

As seen in Fig.3.5 and Table 3.6 the bands similar to that of the monomer are observed in IR spectra of PMCs. However, some shifts occur in frequencies of the polymers because they have different chain length.

Moreover, in FT-IR spectrum of PMC3, the band of C-O-C stretching vibration observed at 1277 cm^{-1} exhibits the mechanism as oxyphenylene radicals are linked to each other during the polymerization. ^{1}H-NMR spectrum of the polymer supports this mechanism as it will be explained later.

3.4.3 ^{1}H-NMR and ^{13}C-NMR spectra of the Polymers

^{1}H-NMR and ^{13}C-NMR spectra of polymers and ^{1}H-NMR spectrum of monomer are shown in Figs. 3.6, 3.7 and 3.8, respectively.

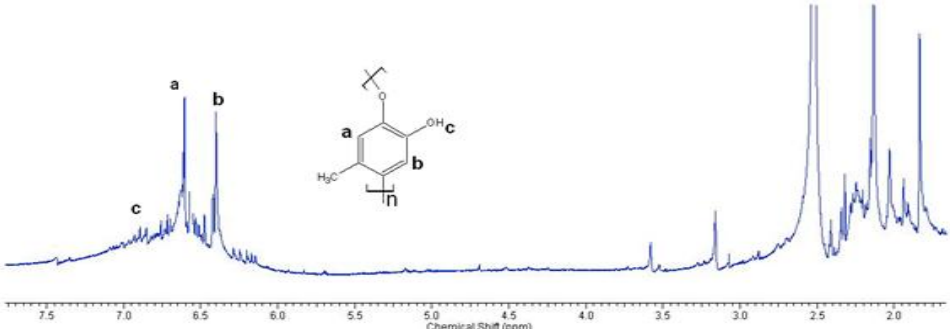


Figure 3.6: ^{1}H-NMR spectrum of PMC.

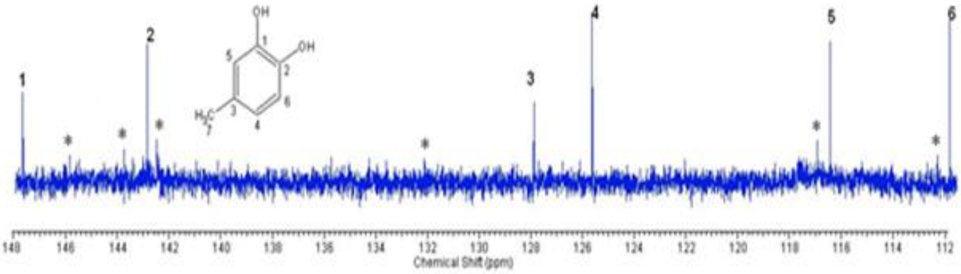


Figure 3.7: ^{13}C-NMR spectrum of PMC.

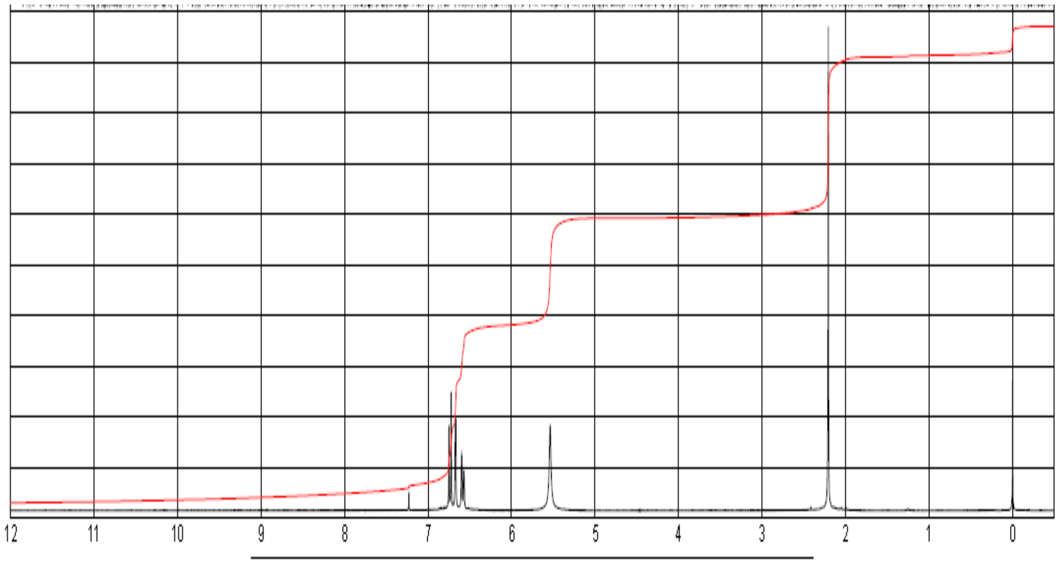


Figure 3.8: ^{1}H-NMR and spectrum of MC.

Characteristic signals of the protons in the aromatic ring,–OH group and the $–CH_3$ group protons are observed in ^{1}H-NMR spectrum of PMC. Also –OH (Single, 1H) at 6.85 ppm, H_a proton (Single, 1H) at 6.77 ppm, H_b proton (Single, 1H) at 6.44 ppm and $–CH_3$ (Single, 3H) at 2.1 ppm signals are observed in the spectrum.

Fig. 3.6 shows ^{1}H-NMR spectrum of PMC. ^{1}H-NMR spectrum of PMC is compared with that of MC to to check if the polymerization completed (Fig. 3.8). As already mentioned before, proton signals of monomers are sharper than those of the polymers, although the broad signals are somehow ambigious in polymerization. Generally speaking 2 dublet and 1 singlet are expected in aromatic region at ^{1}H-NMR spectrum of the monomer whereas 2 singlet are observed in the same region at that of PMC. This confirms that monomer underwent aromatic hydrogen elimination and thus C-C or C-O-C couplings occurred.

Fig. 3.7 shows ^{13}C-NMR spectrum of PMC. There are 7 basic sharp and some low signals at the spectrum. C-7 carbon is observed at 20 ppm (not given here because the spectrum is too wide). C-4 carbon signal observed in the spectrum of monomer shifts to the low frequency area while those of the other carbon signals are practically constant after polymerization. The low intensity signals observed at the spectrum of PMC occurs due to the repeated units in different locations throughout the chain.

3.5 Thermal Stability

The non isothermal TG thermograms of the polymers were recorded, at heating rates of 5, 10, 15, 20°C/min under a nitrogen flow with a flow rate of 10mL/min. They are shown in Appendix 1. A single stage degradation is observed in the thermograms. Initial and final temperatures of the curves, the temperatures corresponding to maximum degradation rate and percent mass loss were determined. It was shown that the initial temperature of the degradation increased with increasing heating rate. Thermal data for the polymers with different molar mass are shown in Table 3.6.

Table 3.6: TG data for the polymers of different oxidants (T_i: Initial degradation temperature ,°C, T_f: Final degradation temperature (°C) T_{max}: The temperature corresponding to maximum degradation rate (°C)).

Heating rate (°C/min)		PMC1	PMC2	PMC3
5	T_i	147	146	146
	T_f	446	443	488
	T_{max}	213	197	208
	%mass loss	44	40	41
10	T_i	154	154	151
	T_f	452	457	503
	T_{max}	214	202	209
	%mass loss	43	40	40
15	T_i	162	161	160
	T_f	454	466	508
	T_{max}	216	211	210
	%mass loss	45	41	42
20	T_i	169	167	167
	T_f	469	475	513
	T_{max}	217	215	211
	%mass loss	45	42	41

3.6 Determination of Kinetic Parameters of Polymers

Thermal degradation kinetics of polymers were investgated by TG. TG-DTG thermograms of polymers with different molar mass exhibit a single degradation stage. The kinetic analysis of the thermogravimetric data was studied by using the methods of the multiple heating rates and of the single heating rate.

WYHC, MKN, CR, MT, HM and vK methods as single heating rate methods, Kissinger, FWO, KAS, Tang and Friedman methods as multiple heating rate methods were used in this study. Also master plot curve method was used to study thermal degradation kinetics of polymers.

The kinetic parameters can be determined by either isothermal or nonisothermal methods. In calculations by using isothermal methods, a little data can be obtained from many TG curves which to interprete is very hard. On the other hand, however, all stages related to solid state degradation reaction, and also degradation temperature and degradation fraction can be seen on a single nonisothermal TG curve. Thus, nonisothermal thermogravimetry is usually preferred in kinetic calculations of solid state reactions.

Two kinds of methods at a constant degradation fraction are used in nonisothermal thermogravimetry one of which based on multiple heating rate (Freeman-Caroll, Ozawa, Friedman) while the other on a single heating rate (Coats-Redfern, MacCallum Taner). There are comparative advantages and disadvantages of them as it is also in isothermal methods. As an example, the results obtained using Freeman-Caroll method are badly scattered thus applying this method to experimental data is very difficult and time consuming i.e. not practical. On the other hand, there are theoretical and practical difficulties related to the single heating rate methods, too.

The activation energy can also be calculated approximately without using particular PC programme only by assumpting the reaction order. However, this can be done precisely by an appropriate PC programme. On the other hand, the activation energy varies with the heating rate the reason why is, however, still under discussion. There are some mathematical and practical difficulties for each method and therefore each one should be interpreted individually.

WYHC, MKN, CR, MT, HM AND Vk as single heating rate and Kissinger, FWO, KAS, Tang and Friedman as multiple heating rate methods were choosen in this study. Variation of the kinetic parameters related to the degradation with the molar mass was also investigated. The most suitable kinetic method was determined for each degradation stage with the calculation of the kinetic parameters related to degradation.

TheTang method which is not dependent on the reaction mechanism was used to calculate the kinetic parameters of the thermal degradation of polymers with different molar mass. The average activation energy values related to thermal degradation of PMC1, PMC2 and PMC3 polymers were found to be 170.6, 128.2 and 119.0 kjmol^{-1}, respectively. The results obtained for PMC1, PMC2 and PMC3 using KAS method are 170.5, 127.4 and 118.6 kjmol^{-1}, respectively.

The average activation energy values of PMC1, PMC2 and PMC3 found by FWO are 169.9, 129.7 and 121.0 kjmol^{-1}, respectively. Another differential method used is Friedman’s. The activation energy values calculated for PMC1, PMC2 and PMC3 are 176.1, 127.8, 121.1 kjmol^{-1}, respectively.

The activation energy values (E) and regression coefficients (R^2) for PMC1, PMC2 and PMC3 which are shown in Tables 3.7-9 were calculated by the related mathematical equations replaced in the PC programme for the four methods. R^2 values found for them are reasonably high.

Table 3.7: Activation energy and regression coefficient values calculated by Tang, KAS, FWO and FR methods for PMC1 (E: Activation energy. R^2: Regression coefficient).

Degradation fraction	TANG		KAS		FWO		FR	
	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2
0.05	81.06	0.9563	80.72	0.9560	83.55	0.9735	86.63	0.9721
0.1	165.4	0.9731	165.0	0.9730	167.1	0.9534	167.5	0.9452
0.2	158.7	0.9516	157.7	0.9511	155.8	0.9976	160.3	0.9678
0.3	160.9	0.9974	160.5	0.9974	160.1	0.9545	163.2	0.9467
0.4	159.3	0.9503	158.8	0.9500	158.3	0.9807	170.7	0.9831
0.5	162.0	0.9787	161.5	0.9786	160.1	0.9959	170.7	0.9911
0.6	159.7	0.9989	161.5	0.9974	159.8	0.9808	171.5	0.9841
0.7	161.6	0.9974	161.1	0.9786	160.1	0.9875	168.3	0.9834
0.8	176.6	0.9787	178.6	0.9839	176.5	0.9812	174.1	0.9865
0.9	231.4	0.9861	230.8	0.9794	229.3	0.9899	240.2	0.9811
0.95	259.6	0.9795	258.9	0.9627	258.5	0.9626	264.6	0.9623
Average	170.6	0.9781	170.5	0.9735	169.9	0.9779	176.1	0.9730

Table 3.8: Activation energy and regression coefficient values calculated by Tang, KAS, FWO and FR methods for PMC2 (E: Activation energy. R^2: Regression coefficient).

Degradation fraction	TANG		KAS		FWO		FR	
	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2
0.05	92.78	0.9913	93.03	0.9912	94.66	0.9925	99.18	0.9881
0.1	115.4	0.9888	115.0	0.9887	119.0	0.9891	121.1	0.9885
0.2	123.0	0.9860	122.6	0.9859	122.6	0.9859	131.5	0.9874
0.3	125.2	0.9903	120.8	0.9894	124.8	0.9892	127.8	0.9993
0.4	132.1	0.9813	131.6	0.9903	132.8	0.9914	136.0	0.9879
0.5	128.2	0.9926	127.8	0.9811	129.4	0.9834	124.3	0.9941
0.6	129.1	0.9943	128.7	0.9926	130.5	0.9935	122.7	0.9728
0.7	125.3	0.9930	124.9	0.9949	127.2	0.9955	124.7	0.9549
0.8	126.7	0.9949	126.2	0.9929	128.8	0.9938	130.6	0.9882
0.9	129.1	0.9923	128.6	0.9943	131.8	0.9951	124.7	0.9785
0.95	183.4	0.9857	182.7	0.9958	185.3	0.9963	164.2	0.9841
average	128.2	0.9901	127.4	0.9906	129.7	0.9914	127.8	0.9840

Table 3.9: Activation energy and regression coefficient values calculated by Tang, KAS, FWO and FR methods for PMC3 (E: Activation energy. R^2: Regression coefficient).

Degradation fraction	TANG		KAS		FWO		FR	
	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2	E (kjmol^{-1})	R^2
0.05	101.8	0.9986	101.4	0.9916	103.2	0.9912	108.7	0.9961
0.1	116.4	0.9917	116.0	0.9939	119.7	0.9835	111.3	0.9623
0.2	100.4	0.9831	100.0	0.9640	101.3	0.9947	107.2	0.9998
0.3	103.5	0.9939	103.1	0.9970	105.4	0.9862	103.5	0.9948
0.4	101.8	0.9956	101.4	0.9542	104.1	0.9894	104.0	0.9988
0.5	101.4	0.9643	101.0	0.9829	103.7	0.9975	104.5	0.9978
0.6	101.3	0.9966	100.9	0.9885	103.9	0.9888	101.0	0.9806
0.7	102.1	0.9923	101.7	0.9867	104.8	0.9847	101.1	0.9749
0.8	111.2	0.9767	110.7	0.9821	113.9	0.9795	116.8	0.9696
0.9	145.6	0.9822	145.0	0.9765	147.4	0.9882	142.5	0.9872
0.95	224.2	0.9868	223.5	0.9885	224.0	0.9880	231.9	0.9985
average	119.0	0.9874	118.6	0.9824	121.0	0.9883	121.1	0.9873

Kinetic parameters of PMC1, PMC2, and PMC3 were also calculated by Kissinger method which is not depend on degradation mechanism. The activation energy and regression coefficient values for PMC1, PMC2, PMC3 were found to be 163.4, 127.7 and 118.4 kj mol^{-1} and 0.9720, 0.9640 and 0.9695, respectively. It can be concluded that the activation energy values were similar for 5 methods (TANG, FWO, KAS, FR, Kissinger) but Kissinger method was not mentioned in the tables since regression coefficient values of this method were lower than other 4 methods. In the beginning of the degradation the activation energy values for PMC1, PMC2 and PMC3 are 80.72, 92.78 and 101.4 kj mol^{-1} respectively whilst they are 264.6, 185.3 and 231.9 kj mol^{-1} for 95% mass loss. Fig. 3.10 shows the activation energy values versus degradation fraction for all polymers.

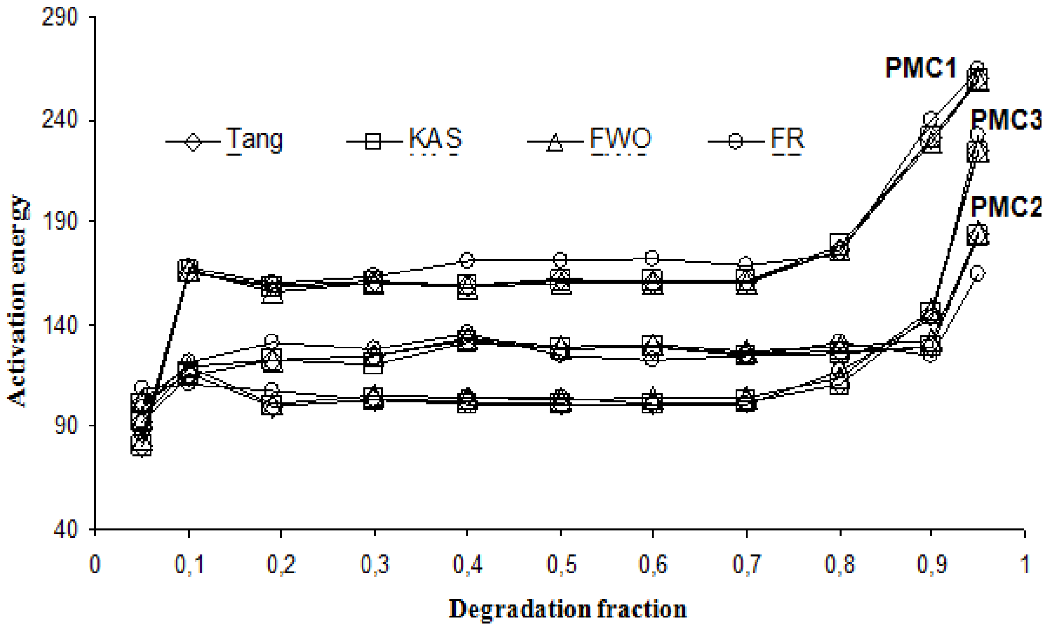


Figure 3.9: The activation energy values versus degradation fraction for PMC1, PMC2 and PMC3.

When Figure 3.10 was examined carefully, it can be seen that the activation energy values are constant in the range of 0.1-0.9 of degradation fraction. Therefore, degradation is not depend on conversional fraction in this range. At the final stage of the study, it was determined that activation energy depends on the heating rate, and it was choosed the most suitable method for the kinetic analysis of polymers. For this purpose, CR, HM, vK, WYHC, MKN and MT methods (based on single heating rate methods) were also used in this study. The data are given in Table 3.10-12.

Table 3.10: Kinetic parameters obtained from TG/DTG curves by various methods at different heating rates for PMC1.

Heating rate		MT	MKN	WHYC	CR	vK	HM
5°C/min	n	5	5	5	5	5	5
	E	113.1	103.5	103.5	103.2	91.59	77.97
	lnA	62.90	24.39	24.31	24.24	24.92	10.62
	R^2	0.9950	0.9944	0.9944	0.9943	0.9930	0.9818
10°C/min	n	5	5	5	5	5	5
	E	113.4	103.7	103.7	103.4	90.37	75.69
	lnA	63.35	24.81	24.74	24.66	24.99	11.09
	R^2	0.9952	0.9945	0.9945	0.9944	0.9923	0.9801
15°C/min	n	5	5	5	5	5	5
	E	117.4	105.1	107.5	107.1	92.21	76.22
	lnA	64.34	25.11	25.69	25.62	25.59	11.21
	R^2	0.9966	0.9961	0.9960	0.9960	0.9927	0.9804
20°C/min	n	5	5	5	5	5	5
	E	**119.06**	109.11	109.11	108.77	92.709	76.032
	lnA	**64.76**	26.17	26.09	26.02	25.79	32.03
	R^2	**0.9977**	0.9973	0.9973	0.9972	0.9938	0.9818

Table 3.11: Kinetic parameters obtained from TG/DTG curves by various methods at different heating rates for PMC2.

Heating rate		MT	MKN	WHYC	CR	vK	HM
5°C/min	n	5	5	5	5	5	5
	E	126.6	117.2	117.2	116.9	105.7	92.24
	lnA	66.66	28.19	28.12	28.06	29.38	11.03
	R^2	0.9887	0.9871	0.9871	0.9870	0.9852	0.9730
10°C/min	n	5	5	5	5	5	5
	E	127.4	115.2	115.2	117.5	104.48	89.63
	lnA	66.99	27.77	27.69	28.35	29.20	11.27
	R^2	0.9917	0.9907	0.9907	0.9905	0.9887	0.9775
15°C/min	n	5	5	5	5	5	5
	E	**129.8**	120.1	120.1	119.8	104.9	88.78
	lnA	**64.93**	28.70	28.62	28.57	29.04	11.02
	R^2	**0.9930**	0.9919	0.9919	0.9918	0.9888	0.9767
20°C/min	n	5	5	5	5	5	5
	E	131.9	122.1	122.1	121.8	105.2	87.85
	lnA	68.00	29.44	29.36	31.61	29.43	11.39
	R^2	0.9928	0.9917	0.9917	0.9917	0.9889	0.9769

Table 3.12: Kinetic parameters obtained from TG/DTG curves by various methods at different heating rates for PMC3.

Heating rate		MT	MKN	WHYC	CR	vK	HM
5°C/min	n	5	5	5	5	5	5
	E	123.7	114.2	114.2	113.9	102.3	88.76
	lnA	66.38	27.91	27.83	30.06	28.85	32.13
	R^2	0.9928	0.9912	0.9912	0.9911	0.9833	0.9667
10°C/min	n	5	5	5	5	5	5
	E	127.1	117.5	117.5	117.2	104.0	89.2
	lnA	67.41	28.99	28.84	28.78	29.58	30.12
	R^2	0.9938	0.9924	0.9924	0.9923	0.9856	0.9702
15°C/min	n	4.7	4.9	4.9	4.9	5	5
	E	**122.8**	118.7	118.7	118.4	106.7	91.04
	lnA	**66.06**	29.03	28.95	28.90	30.28	30.13
	R^2	**0.9952**	0.9942	0.9942	0.9942	0.9892	0.9762
20°C/min	n	4.8	5	5	5	5	5
	E	125.9	121.6	121.6	121.3	105.0	89.08
	lnA	36.83	29.68	29.60	29.55	29.73	11.68
	R^2	0.9944	0.9933	0.9933	0.9932	0.9879	0.9741

The method which exhibited a regression coeffient closest to 1 was accepted the optimum one which is MT of the single heating rate. It was shown that the activation energy values found by single heating rate methods were lower than those found by multiple heating rate methods for PMC1 presumably due to the reaction order which was accepted constant. This is not valid for PMC2 and PMC3 as their activation energies determined by both single and multiple heating rate methods are similar.

3.7 Computer

In this study, such an algorithmic computer programme was used and it was applied to the thermal degradation of several polymers the webbased software. **Thermal Analysis Version 1.0.0**. was developed in PHP web programming language in order to make kinetic analyses of pyrolysis and oxidation reactions from the results of TG analysis. Among the results of TG analysis, the temperature and first differential values corresponding to the degree of conversion are used as data by the software.

Using the integral methods such as CR, HM, FWO and differential methods such as vK, KSG, FR and difference-differential methods such as FC and MC; the software **Thermal Analysis Version 1.0.0**. calculates reaction order, n, activation energy, E, and pre-exponential factor, A, with standard deviation for pyrolysis and oxidation reactions according to manual and automated procedures. The kinetic parameters are calculated according to each method individually in the manual system whereas in the automated system, the optimal method and kinetic parameters related to it may be used followed comparisons of linear regression coefficients of Arrhenius plots obtained from each method. Consequently, it will be possible:

•To collect and summarize several kinetic methods reported in the literature,

•To create a software that will be submitted to the literature to constitute a very important source for the the investigators of the area,

•To save time and labor through eliminating the time-consuming and laborious processes of obtaining kinetic and thermodynamic parameters by transferring the kinetic models to the WEB,

•To obtain the results that will be very important in terms of enhancing the reliability of the thermal method by the virtue of more robust comparisons of the obtained kinetic and thermodynamic parameters.

Data entry to the software is in interactive manner or by copy-andpaste procedure. The software includes various isothermal functions and the CR function. There are three procedures to choose the related mechanisms of reactions. Accordingly;

•The best model is defined either by the user

•Or by the system according to optimal linearity for single or multiple curve.

•And in case of more than one possible models all are applied and the suitable results may be saved and printed.

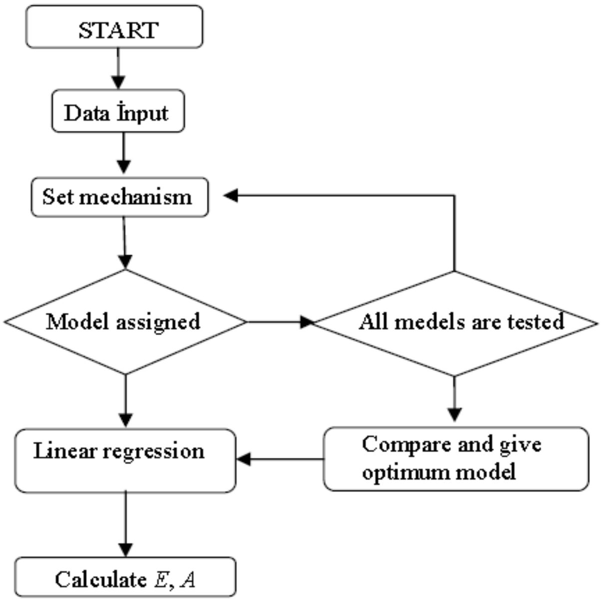


Figure 3.10: Simplified block diagram of isothermal subroutine of Thermal Analysis Ver. 1.0.0.

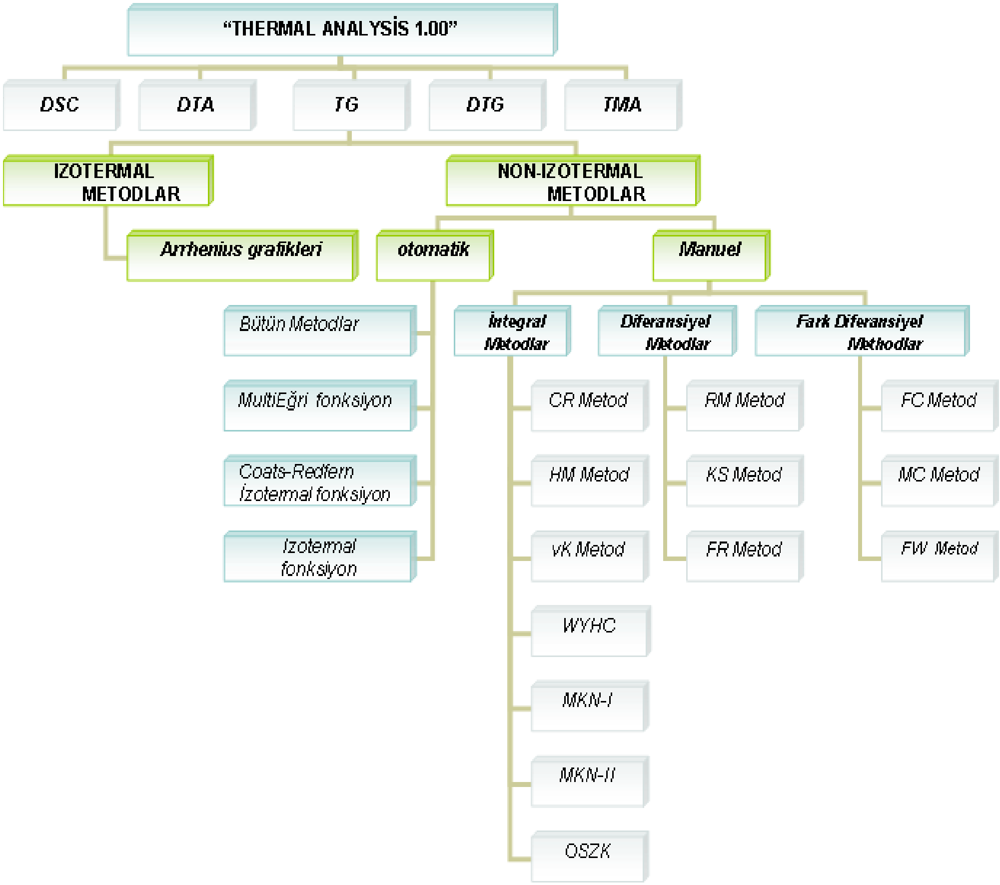
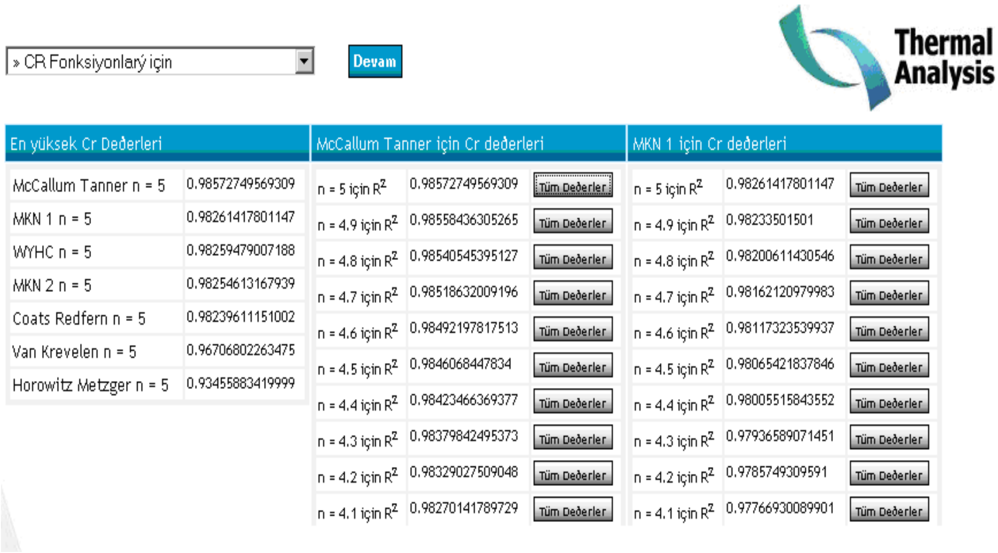


Figure 3.11: Kinetic methods (CR, HM, vK, Ozawa-Zsako, WYHC, MKN, Kissinger, Friedman, Freeman-Carroll, MT, Romero, FWO).



En yüksek Cr Değerleri	
McCallum Tanner n = 5	0.98572749569309
MKN 1 n = 5	0.98261417801147
WYHC n = 5	0.98259479007188
MKN 2 n = 5	0.98254613167939
Coats Redfern n = 5	0.98239611151002
Van Krevelen n = 5	0.96706802263475
Horowitz Metzger n = 5	0.93455883419999

McCallum Tanner için Cr değerleri		
n = 5 için R^2	0.98572749569309	Tüm Değerler
n = 4.9 için R^2	0.98558436305265	Tüm Değerler
n = 4.8 için R^2	0.98540545395127	Tüm Değerler
n = 4.7 için R^2	0.98518632009196	Tüm Değerler
n = 4.6 için R^2	0.98492197817513	Tüm Değerler
n = 4.5 için R^2	0.9846068447834	Tüm Değerler
n = 4.4 için R^2	0.98423466369377	Tüm Değerler
n = 4.3 için R^2	0.98379842495373	Tüm Değerler
n = 4.2 için R^2	0.98329027509048	Tüm Değerler
n = 4.1 için R^2	0.98270141789729	Tüm Değerler

MKN 1 için Cr değerleri		
n = 5 için R^2	0.98261417801147	Tüm Değerler
n = 4.9 için R^2	0.98233501501	Tüm Değerler
n = 4.8 için R^2	0.98200611430546	Tüm Değerler
n = 4.7 için R^2	0.98162120979983	Tüm Değerler
n = 4.6 için R^2	0.98117323539937	Tüm Değerler
n = 4.5 için R^2	0.98065421837846	Tüm Değerler
n = 4.4 için R^2	0.98005515843552	Tüm Değerler
n = 4.3 için R^2	0.97936589071451	Tüm Değerler
n = 4.2 için R^2	0.9785749309591	Tüm Değerler
n = 4.1 için R^2	0.97766930089901	Tüm Değerler

Figure 3.12: An example page of the PC programme.

4 CONCLUSION

FT-IR spectra of polymers synthesized by oxidative polycondensation method was in accord with FT-IR spectrum of polycatechol in literature (N. Aktaş, 2003, S. Dubey) which means that PMC is a catechol derivative and synthesized as oxiphenylene units linked through 1 and 4 positions.

2 dublet and 1 singlet peaks observed in ^{1}H-NMR and ^{13}C-NMR spectra of monomer are due to the aromatic proton signals of MC while the 2 singlet over the aromatic region confirm the existence of proposed 1,4 oxyphenylene binding occurs after polymerization. Low intensity signals observed in ^{1}H-NMR spectrum correspond to the proton signals of the terminal units.

The polymers were analysed by TG-DTA, size exclusion chromotography (SEC) and solubility determination tests. PMC1, PMC2 and PMC3 were obtained with the yields of 75, 44 and 18 percent, respectively under optimum reaction conditions. The values of number average molar mass (M_n), weight average molar mass (M_w) and polydispersity indexes (PDI) of PMC1, PMC2 and PMC3 were found to be 9600, 11600 gmol^{-1}, 1.208 and 8800, 9700 gmol^{-1}, 1.102 and 7100, 8200 gmol^{-1}, 1.154, respectively.

As a result of kinetic studies, the MacCallum Tanner was found as the most convinient kinetic method for PMC1 at 20°C/min; and for PMC2 and PMC3 at 15°C/min.

PMC1 has had the highest molar mass while PMC3 has the lowest one. The activation energies of thermal degradation of PMC1, PMC2 and PMC3 by TANG method based on multiple heating rate were found to be 170.6, 128.2 and 119 kjmol^{-1},respectively showing that the activation energy increased with the increasing molar mass as it is already expected. The activation energies determined for PMC1, PMC2 and PMC3 by MT method were found to be 119.06, 129.8 and 122.8 kjmol^{-1}, respectively. It is concluded that the activation energy did not increase with the increasing molar mass for single heating rate methods which means that the multiple heating rate methods are more convenient than those of single heating rate for polymer degradation.

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6 CURRICULUM VITAE

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7 APPENDIX 1

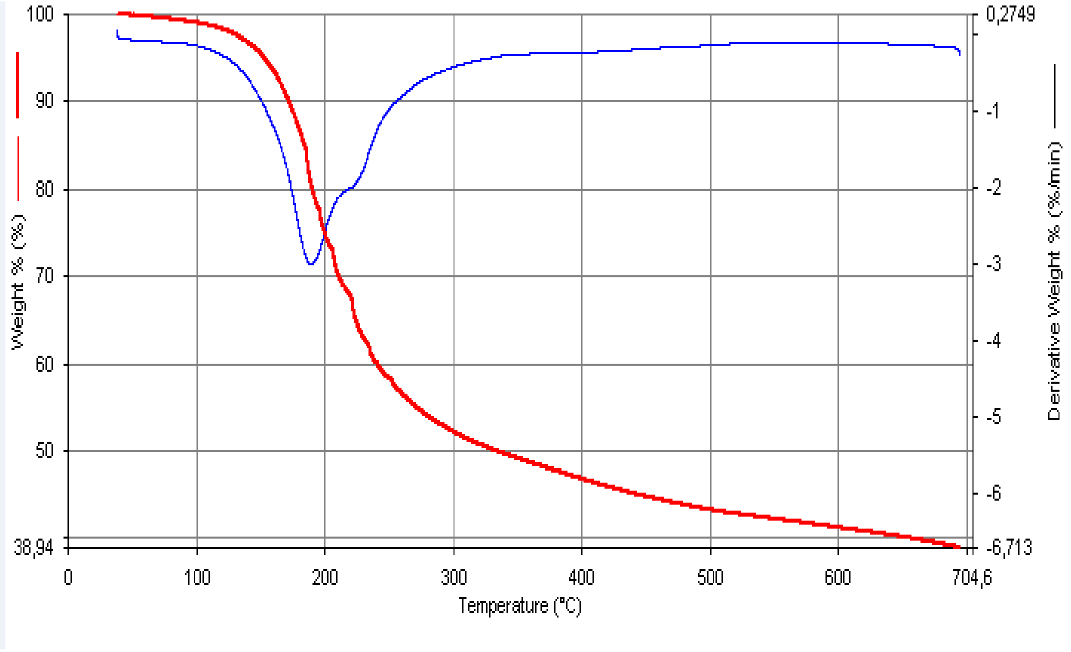

Figure A.1: TG-DTG curve of PMC1 at a heating rate of 5°C in nitrogen atmosphere.

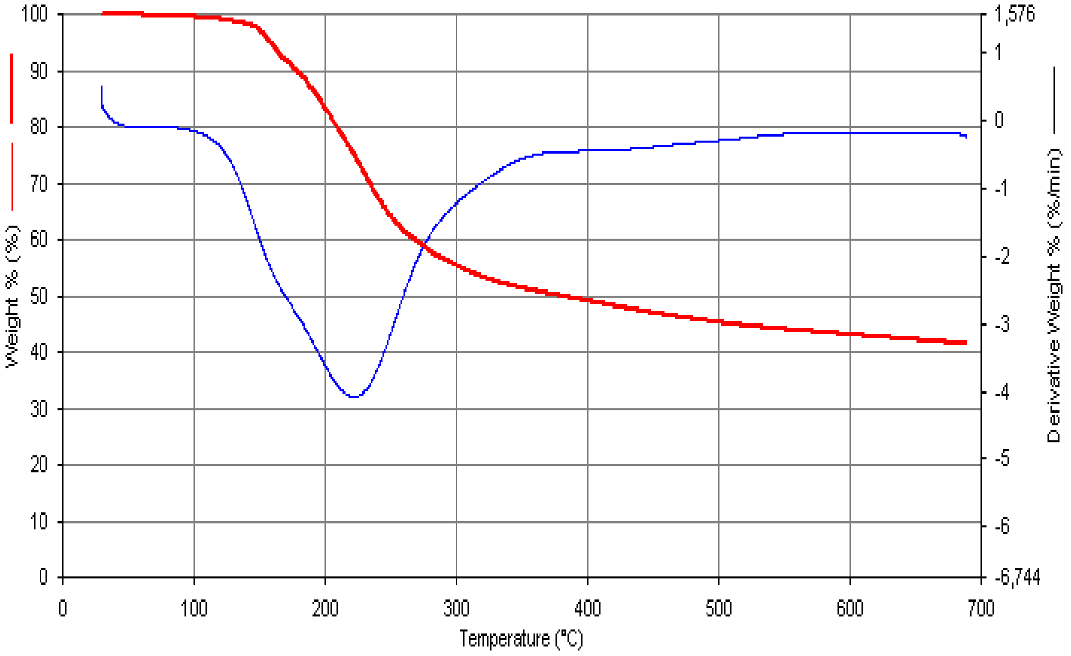

Figure A.2: TG-DTG curve of PMC1 at a heating rate of 10°C in nitrogen atmosphere.

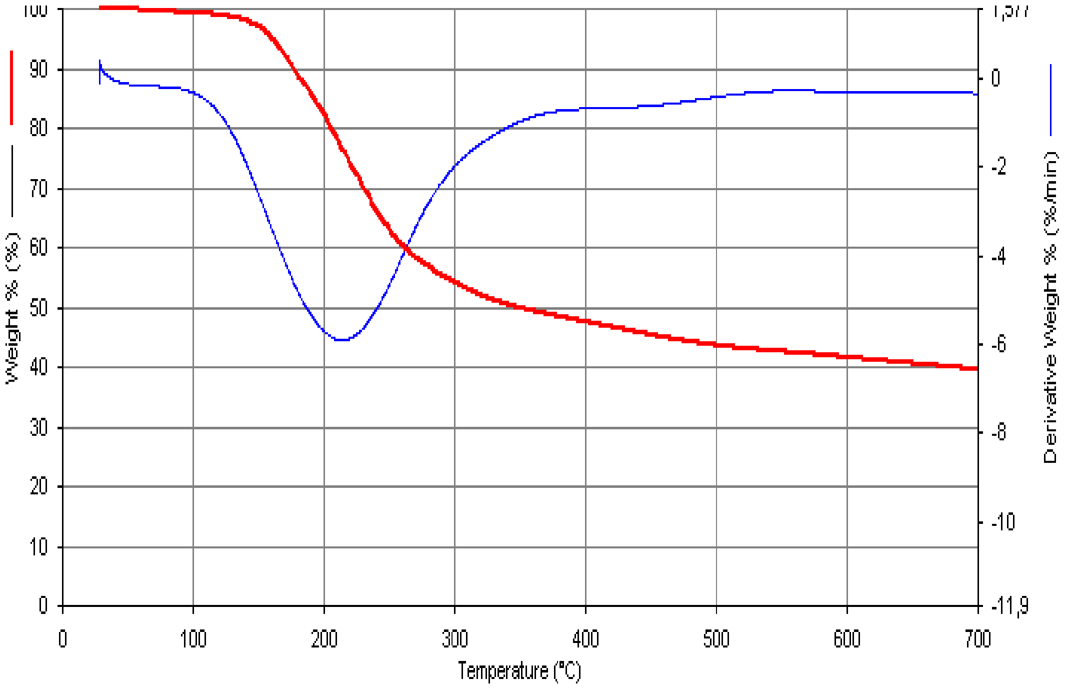

Figure A.3: TG-DTG curve of PMC1 at a heating rate of 15°C in nitrogen atmosphere.

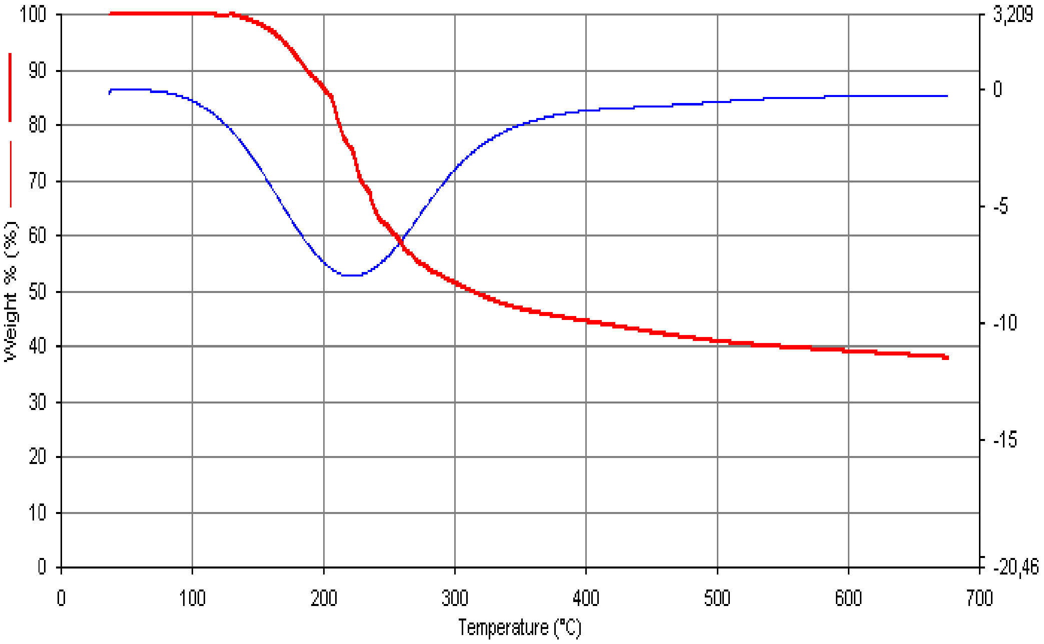

Figure A.4: TG-DTG curve of PMC1 at a heating rate of 20°C in nitrogen atmosphere.

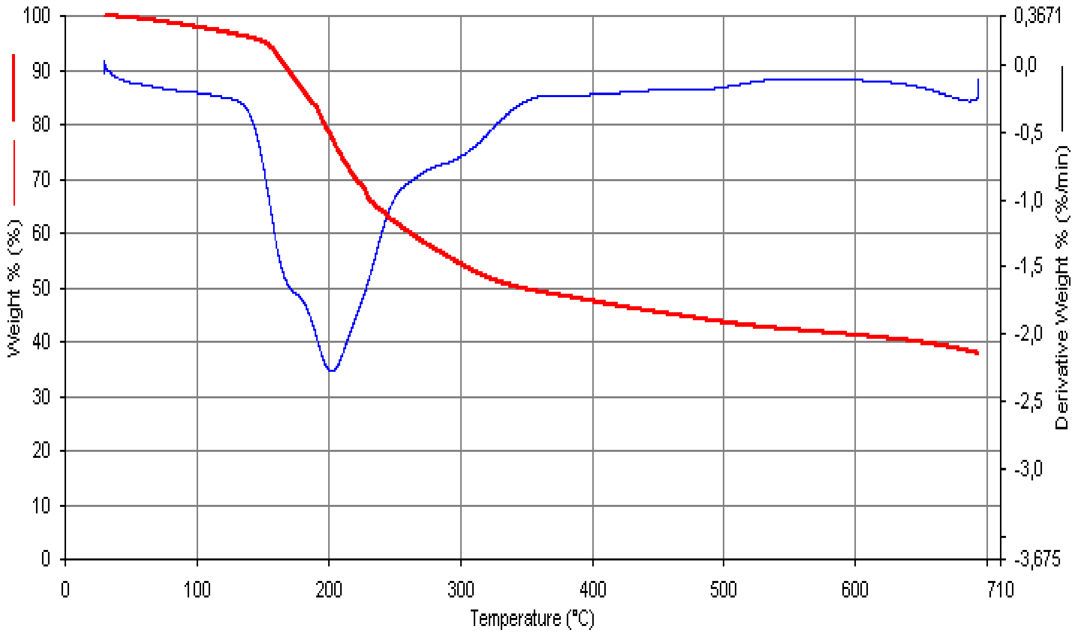

Figure A.5: TG-DTG curve of PMC2 at a heating rate of 5°C in nitrogen atmosphere.

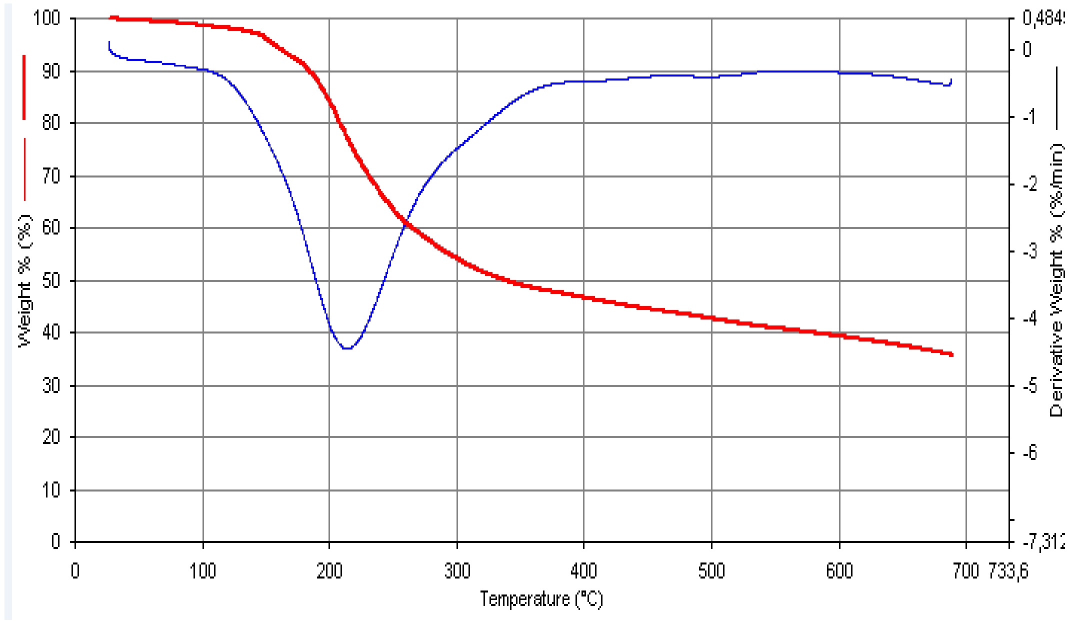

Figure A.6: TG-DTG curve of PMC2 at a heating rate of 10°C in nitrogen atmosphere.

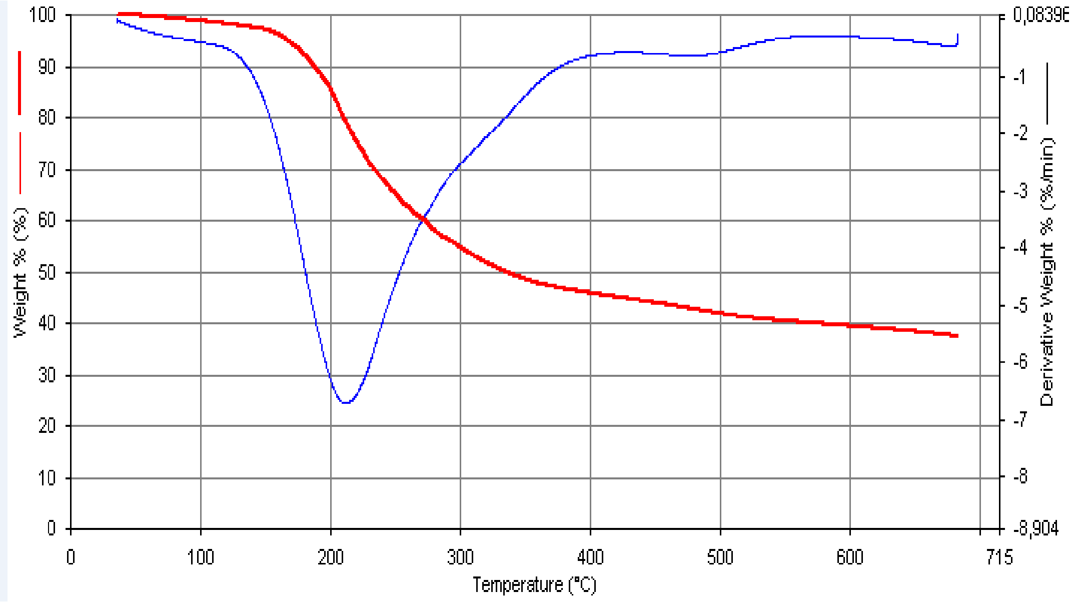

Figure A.7: TG-DTG curve of PMC2 at a heating rate of 15°C in nitrogen atmosphere.

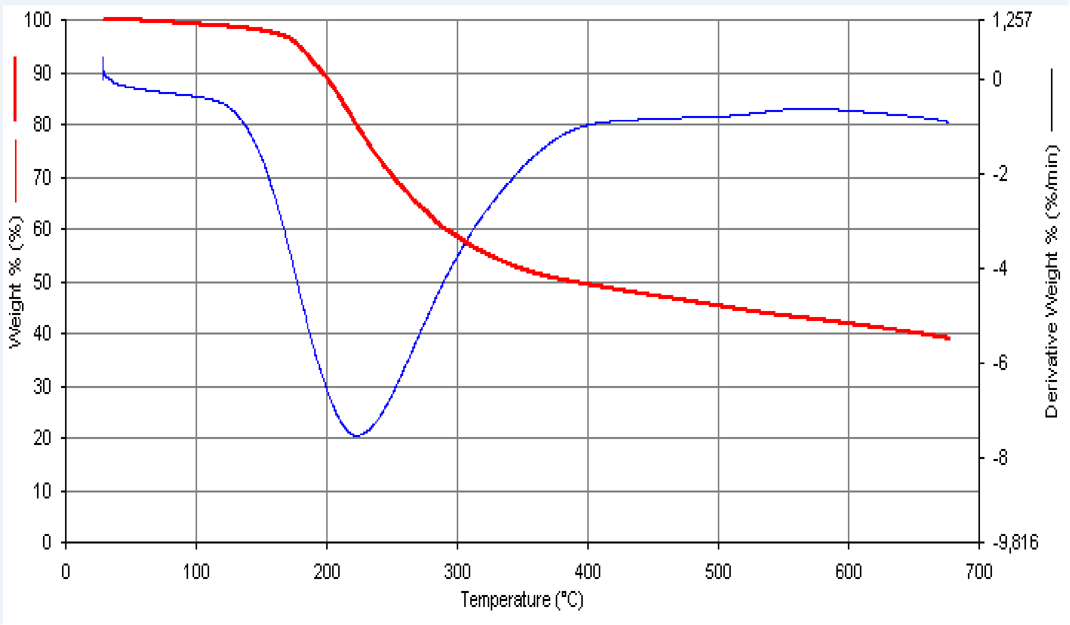

Figure A.8: TG-DTG curve of PMC2 at a heating rate of 20°C in nitrogen atmosphere.

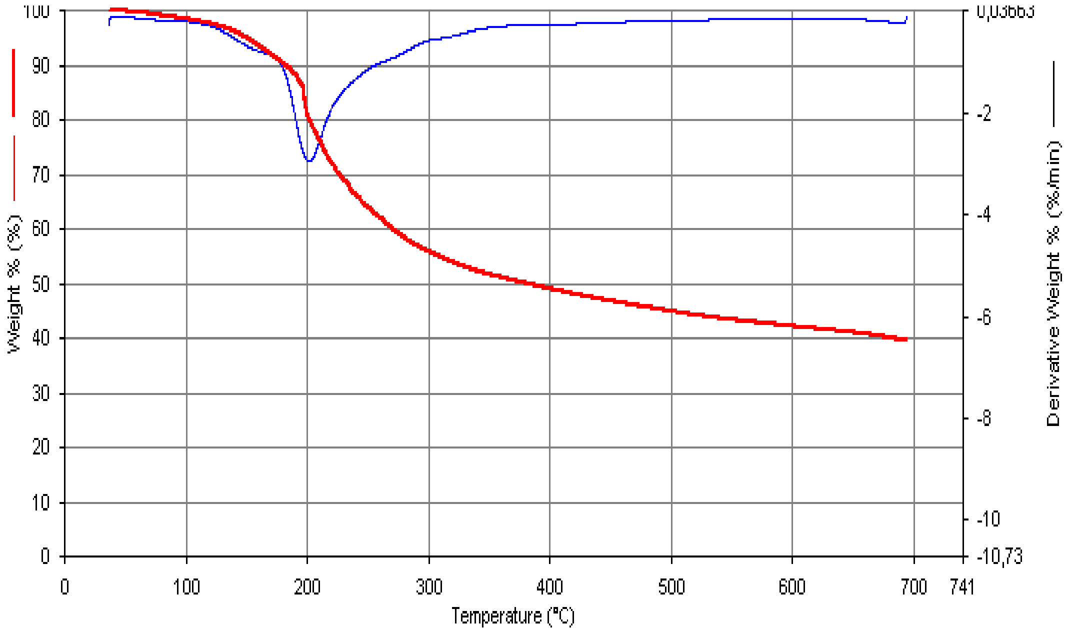

Figure A.9: TG-DTG curve of PMC3 at a heating rate of 5°C in nitrogen atmosphere.

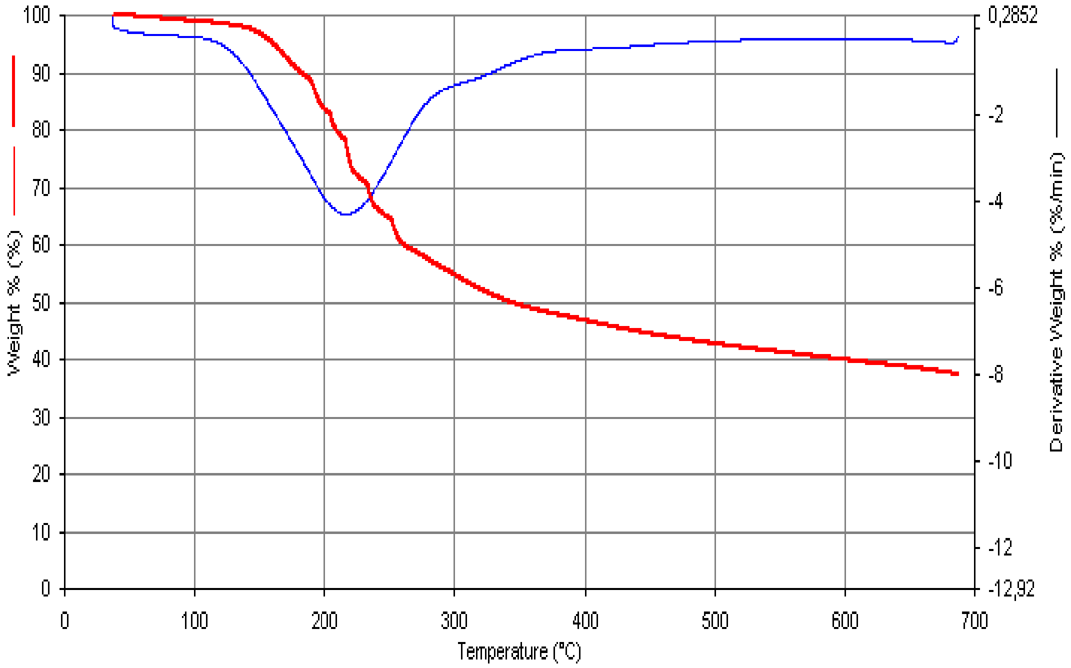

Figure A.10: TG-DTG curve of PMC3 at a heating rate of 10°C in nitrogen atmosphere.

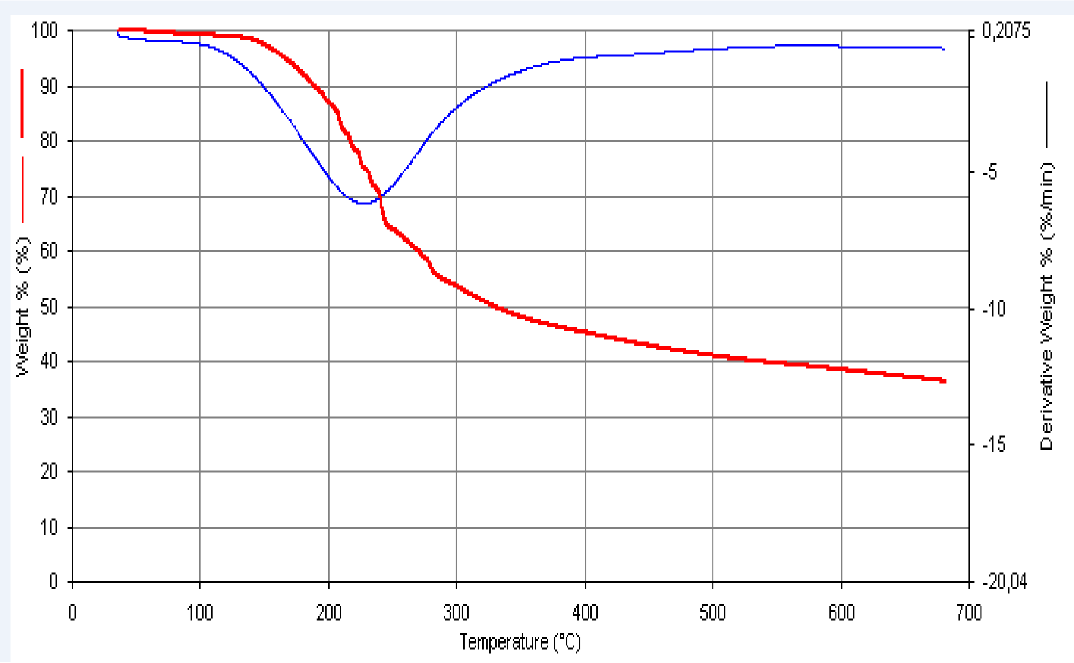

Figure A.11: TG-DTG curve of PMC3 at a heating rate of 15°C in nitrogen atmosphere.

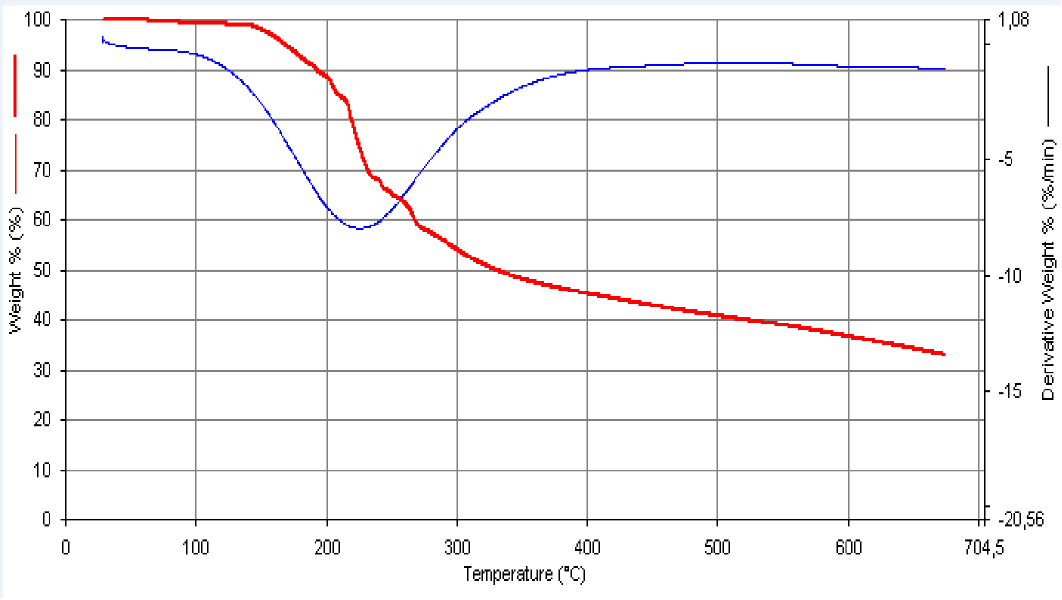

Figure A.12: TG-DTG curve of PMC3 at a heating rate of 20°C in nitrogen atmosphere.