



The Accuracy of Approximation Equations in the Study of Thermal Decomposition Behaviour of Some Synthesized Optically Active Polyamides

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ABSTRACT

This paper reports on the accuracy of the integral methods used for the kinetic analysis of degradation of synthesized optically active polyamides. For this purpose, thermogravimetric analysis is a technique, widely used in polymer science because of its simplicity. On analyzing data by integral methods, it is necessary to calculate the temperature integral, which does not have an analytical solution. Instead of performing the numerical integration, most of the researchers prefer to avoid the problem by using approximate expressions, not always adequate and several hundreds of citations to the original papers can be found in recent polymer science publications. The most important application of these equations is the determination of the kinetic parameters, in particular activation energies, and not the computation of the Arrhenius integral. A methodical analysis of the errors involved in the determination of the activation energy from these integral methods is invisibly missing. A comparative study on the precision of the activation energy as a function of u and T computed from different integral methods has been carried out. Furthermore, for a series of optically active polyamides, the interpretation of kinetic parameters (E , ΔS , ΔG and ΔH) of thermal decomposition stages has been evaluated and reported.

Key Words:

error analysis;
kinetic study;
thermal stability;
optically active polyamides.

INTRODUCTION

Throughout the literature, there are many papers concerning the synthesis and characterization of different novel high performance polymers. Nevertheless, only a small amount of work has been published on the thermal behaviour and kinetic analysis of the polymers [1-3]. The determination of the kinetic parameters of the polymers provides important additional information for their use and applications as new materials. Thermogravimetry (TG) has been widely

used for such studies. Experiments are usually performed under linear heating rate programme. In the TG experiment, the recorded magnitude, for example mass loss, is proportional to the extent of the reaction (α).

The TG data can be used for obtaining the kinetic parameters of the thermal degradation of the polymer sample [4-7]. To do the kinetic study of the integral curve (mass loss vs. temperature) directly obtained from thermogravimetric

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analysis, it is necessary to use an integral analysis method. A restriction of the integral methods of kinetic analysis is that the temperature integral does not have a precise analytical solution for linear heating rate programme. Many authors have employed different computational methods among which the Coats-Redfern, Van-Krevelen and Horowitz-Metzger methods are well known and have been tested by several researchers. Still, there are some constant misgivings about their accuracy for the original kinetic parameters, because of their lack of accuracy in the estimation of the temperature integral [8-24].

Thermally stable polyamides (PA)s have received much attention over the past decade, owing to increasing demands for high-performance polymers materials for several applications such as high strength, high-modulus fibres, high-temperature coating and high-efficiency semi-permeable membranes. But, due to their low solubility, their applications have been restricted [25-28]. Much effort has been made to create structurally modified aromatic polymers having better characterization in terms of both solubility and processability with retention of their high thermal stability. Introduction of flexible chains into the PAs backbone, the use of meta-oriented monomers and synthesis of PAs with non-coplanar unit in the polymer chains, resulted in a number of modified PAs. Another strategy is based on the introduction of bulky side groups into the polymer chains [29-31]. The combinations of amino acid residues into synthetic PAs, only those containing the naturally occurring (L)- α -amino acids, being structurally close to the natural polypeptides, possess potentially degradable linkages that make them suitable as biomaterials and therefore are classified under environmentally friendly polymers. Since the resulting polymers are optically active and have good thermal stability they are potentially capable to be used as a chiral stationary phase in chromatography technique for the separation of racemic mixtures [32-36].

1,8-Naphthalene derivatives have been widely investigated in the last decade because of their potential technological use in electronic and opto-electronic tools. Naphthalene structure as a chromophore imparts special characteristics such as

moisture resistance, bulky, rigid and low coefficient of thermal expansion to polymer. The insertion of naphthalene as a pendant group in a polymer chain has resulted in decreased crystallinity, enhanced solubility and thermal stability [37-40].

This article describes a successful synthesis of optically active PAs which were prepared by direct polycondensation reactions from chiral dicarboxylic acid with various diisocyanates under conventional heating. In another important part of this research, a comprehensive study of the thermal decomposition behaviour of obtained polymer using approximation of the different integral methods proposed by Coats-Redfern, Doyle, Van-Krevelen, Horowitz-Metzger, Gyulai-Greenhow and MacCallum-Tanner with emphasis on the accuracy of such approximation to the temperature integral for the determination of the kinetic parameters was performed. The calculated errors are checked both, with simulated (Mathcad software 14.0) and experimental curves.

THEORETICAL CONSIDERATION

Before the error analysis of integral methods, a new classification of the methods was proposed to divide them into two types. (A): Coats-Redfern, Doyle, Van-Krevelen and Horowitz-Metzger equations (eqn) as a function of $u = E/RT$ values, taken as the accurate data for computation of the integral. (B): the mathematical results from equations Gyulai-Greenhow and MacCallum-Tanner indicate that the value of integral depends not only on the value of u but also on the particular value of the temperature, T [1-18]. The methods of calculation of the kinetic parameters of solid state reactions from non-isothermal data are usually based upon the following relationship:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-(E/RT)} f(\alpha) \quad (1)$$

where α is the reacted fraction, A is Arrhenius pre-exponential factor, E is the activation energy, R is the gas constant, β is the heating rate and $f(\alpha)$ is a function depending on the reaction mechanism. After logarithmic derivation it can be rearranged in the following form:

$$\ln \frac{(d\alpha/dT)}{f(\alpha)} = \ln A - \ln \beta - \frac{E}{RT} \quad (2)$$

Eqn (1) cannot be directly integrated under rising temperature conditions unless the temperature is a known function of time. If the degradation of polymers is recorded under a linear heating rate $\beta = dT/dt$, the integration of eqn (1) leads to eqn (3).

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-(E/RT)} dT \quad (3)$$

After performing the variable change $u = E/RT$, eqn (3) may be rearranged in the following way:

$$g(\alpha) = \frac{AE}{\beta R} \int_u^\infty \frac{e^{-u}}{u^2} du = \left(\frac{AE}{\beta R} \right) p(u) \quad (4)$$

$$p(u) = \int_u^\infty \frac{e^{-u}}{u^2} du \quad (5)$$

or in logarithmic form (eqn (6)):

$$\ln g(\alpha) = \ln \left(\frac{AE}{\beta R} \right) + \ln p(u) \quad (6)$$

The value of $p(u)$ is calculated by numerical integral. The $p(u)$ function does not have an exact analytical solution, and many approximations for the $p(u)$ function have been proposed for performing the kinetic analysis of solid-state reactions [1-9].

For solution of type (A) Coats-Redfern, Doyle, Van-Krevelen and Horowitz-Metzger equations have been employed: for at first Coats-Redfern approximation for eqn (3) was used which provided eqn (7):

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (7)$$

Since E is in kcal/mol, $2RT/E \ll 1$ [15,23,24], eqn (7) is reduced to eqn (8):

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \left(\frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (8)$$

where $g(\alpha)$ is a degradation process function.

A plot of $\ln g(\alpha)/T^2$ vs. $1/T$ should give a slope

from which an energy of activation can be calculated. This method requires only the relative mass of the sample, from which $g(\alpha)$ is determined as a function of reaction temperature to determine the activation energy of the reaction.

In the Van-Krevelen method, a temperature T_M is a reference temperature, usually it is the temperature at which the reaction rate is maximum, which is measured from the peak in the differential thermal analysis curve (eqn (9)) [3-6].

$$\ln g(\alpha) = \ln B + \left(\frac{E}{RT_M} + 1 \right) \ln T \quad (9)$$

where B is determined as follows:

$$B = \frac{A}{\beta} \left(\frac{E}{RT_M} + 1 \right)^{-1} \left(\frac{0.368}{T_M} \right)^{\frac{E}{RT_M}} \quad (10)$$

Horowitz-Metzger simplified the exponential integral using an approximation similar to Van-Krevelen, defining a characteristic temperature θ (K) such that $\theta = T - T_S$, where T_S is an arbitrary reference temperature. They finally obtained eqn (11).

$$\ln g(\alpha) = \left(\frac{E\theta}{RT_S^2} \right) \quad (11)$$

In eqn (11) it is assumed that $\ln g(\alpha)$ is a linear function of θ , and thus of the temperature and allows the activation energies to be determined from the slopes [6,7].

Doyle calculated $\ln g(\alpha)$ values for a wide range of u values, and found that within the limits $20 \leq u \leq 60$ the following approximation applies in eqn (12):

$$\ln g(\alpha) = \ln \left(\frac{AE}{\beta R} \right) - \left(\frac{1.052E}{RT} \right) - 5.334 \quad (12)$$

The apparent activation energy, E (kcal/mol), can therefore be obtained from a plot of $\ln g(\alpha)$ against $1/T$ (T is the temperature in K), for the fixed α , the slope of such a line is given by $(-1.052 E/R)$ [17,18].

For type (B) Gyulai-Greenhow and MacCallum-Tanner approaches were used as follows: the isoconversional integral method is based on the

Gyulai-Greenhow approximation of the temperature integral. It is shown in eqn (13):

$$\ln g(\alpha) = \ln \left(\frac{A}{\beta} \right) + a - b \ln E - \left(\frac{cE^d}{T} \right) \quad 20 \leq u \leq 60 \quad (13)$$

where in eqn (13), $a = 8.1614$, $b = 0.915784$, $c = 621.302$ and $d = 0.95823$ are constant parameters.

The method established by MacCallum-Tanner, derived the following equation (eqn (14)):

$$\ln g(\alpha) = \ln \left(\frac{AE}{\beta R} \right) - 1.1124 E^{0.4351} - \left(\frac{449 + 217E}{0.434T} \right) \quad (14)$$

Moreover, these equations proposed a kind of approximations of $p(u)$ through integration over small temperature intervals to enhance the accuracy [22]. In the evaluation of the temperature integral, an important point is that it should not be regarded as a pure mathematical problem, but should be considered in connection with the aim of kinetic analysis, i.e. accurate extraction of kinetic parameters and model description. Any approximation leading to accurate enough evaluation of the kinetic parameters should be regarded as reasonable. In this sense, some approximations with higher mathematical complexities may have no remarkable advantage over some other simple approximations. With this idea in mind, this paper proposes a new consideration on the published approximations and compares them by examining their performances in kinetic analysis, whereby the integral methods are evaluated and compared in terms of error analysis.

Error Analysis of the Integral Methods

In this section, the error analysis of kinetic parameters was conducted for the above mentioned two types of integral methods. The integral of the Arrhenius equation does not have an exact solution and therefore this expression cannot be expressed in a closed form. Several approaches have been proposed in the literature for the integral of the Arrhenius equation in order to determine the activation energy from experimental integer data [1-18], for example, eqn (1) cannot be directly integrated under rising temperature conditions unless the temperature was a known function of the time.

Eqn (1) would also be written in the following form (eqn (15)):

$$g(\alpha) = \frac{A}{\beta} I \quad (15)$$

where I stands for the integral of the Arrhenius equation. Eqns (3) and (15) allow the direct analysis of the experimental data obtained from the measurement of the evolution of an integral magnitude, such as the mass loss recorded in a thermobalance as a function of the temperature under a linear heating programme. Instead of the exact eqn (15) the use of these approximations is realized by calculating the activation energy through the following equation:

$$g(\alpha) = \frac{A}{\beta} I_a \quad (16)$$

In general, the approximations to the temperature integral have been chosen in such a way that the plot of the logarithm of the corresponding $g(\alpha)$ function vs. a function of temperature $f(T)$ leads to a straight line with a slope which is used to determine the activation energy:

$$\frac{d \ln g(\alpha)}{df(T)} = f(E_a) \quad (17)$$

The corresponding approximate Arrhenius integral functions, I_a , $f(T)$ and $f(E_a)$ listed in Table 1 depend on the considered approximation to the Arrhenius integral and the (a) stands as its approximate subindex [10-15]. The relative error, ε , of the activation energy (E_a) calculated by the different approximated equations can be defined by the following equation (eqn (18)):

$$\varepsilon(\%) = \left(\frac{E_a - E}{E} \right) 100 = \left(\frac{E_a}{E} - 1 \right) 100 \quad (18)$$

By differentiating the logarithmic form of eqn (14) with regards to $f(T)$ we obtain eqn (19).

$$\frac{d \ln g(\alpha)}{df(T)} = \frac{d \ln I}{df(T)} \quad (19)$$

Table 1. Functions I_a corresponding to the approaches of different integral methods of the Arrhenius equation and their related functions $f(T)$, $f'(T)$ and $f(E_a)$ as defined by eqn (17) [5-8].

Method	I_a	$f(T)$	$f'(T)$	$f(E_a)$
Coats-Redfern	$\frac{e^{-(E_a/RT)}}{(E_a/RT^2)}$	$1/T$	$-T^{-2}$	$-2T - \frac{E_a}{R}$
Doyle	$(E_a/R) e^{-\left(\frac{1.052E_a}{RT}\right)} e^{-5.334}$	$1/T$	$-T^{-2}$	$-\frac{1.052E_a}{R}$
Van-Krevelen	$\left(\frac{0.368}{T_M}\right)^{\frac{E_a}{RT_M}} \left(\frac{E_a}{RT_M} + 1\right)^{-1} T^{\left(\frac{E_a}{RT_M} + 1\right)}$	$\ln(T)$	$1/T$	$\frac{E_a}{R} + 1$
Horowitz-Metzger	$(\beta/A) e^{\left(\frac{E_a\theta}{RT_S^2}\right)}$	θ	1	$\frac{E_a}{R} + T_S^2$
Gyulai-Greenhow	$e^{8.1614} E_a^{-0.915784} e^{-\left(\frac{621.302E_a^{0.95823}}{T}\right)}$	$1/T$	$-T^{-2}$	$-621.302E_a^{0.95823}$
MacCallum-Tanner	$(E_a/R) e^{-\left(1.1124E_a^{0.4351}\right)} e^{-\left(\frac{449+217E_a}{0.434T}\right)}$	$1/T$	$-T^{-2}$	$-1034.56 - 500E_a$

(a) T_M is a reference temperature: usually it is the temperature at which reaction rate is a maximum; (b) $\theta = T - T_S$, being T_S temperature at the point of inflection in TG curve.

By combining eqns (17) and (19), eqn (20) is obtained, where $df(T) = f'(T) \times dT$.

$$\frac{d \ln I}{df(T)} = f(E_a) \quad (20)$$

By introducing the variable $u = E/RT$, it is shown that the derivative of $f(T)$ is connected with the derivative of u through the following expression:

$$-df(T) = \frac{R}{E} f'(T) T^2 du \quad (21)$$

Thus, from combination of eqns (20) and (21), eqn (22) is obtained.

$$-\frac{d \ln I}{du} = \frac{R}{E} f'(T) T^2 f(E_a) \quad (22)$$

The value of E_a/E is a function of u , therefore in order to obtain the amount of $d \ln I/du$ from eqn (22), it is imperative to use the substituted $f(E_a)$ and $f'(T)$ corresponding to the different approximated

equations which are tabulated in Table 1. Finally, after substituting the expressions for E_a/E into eqn (18), the error functions listed in Table 2 are obtained for the Coats-Redfern, Doyle, Van-Krevelen, Horowitz-Metzger, Gyulai-Greenhow, and MacCallum-Tanner approaches, respectively [1-24]. The error expressions shown in Table 2 indicate that the errors in the activation energy depend on the values of $u = E/RT$ for all the six approximation equations. The values of percentage ϵ tabulated in Tables 3-5 for the different approaches have been calculated as a function of u after calculating the corresponding values of $d \ln I/du$ by numerical methods using the Mathcad software with a tolerance better than 10^{-9} . It is clear from these tables that the errors significantly change as a function of u . The mathematical form of eqns (13) and (14) indicates that the value of $p(u)$ given by the approximations of Gyulai-Greenhow and MacCallum-Tanner depends not only on the value of $u = E/RT$ but also on the value of the temperature, T . The value of the error, percentage ϵ obtained as a function of these two variables from eqns (13) and (14), are shown in Tables 4 and 5. The results

Table 2. Expressions for the relative errors of the approximation as calculated from different approximations of the Arrhenius integral [5-8].

Approximation	Relative error	Range
Coats-Redfern	$\varepsilon(\%) = \left[-\left(\frac{d \ln I}{du} \right) - \frac{2}{u} - 1 \right] 100$	-
Doyle	$\varepsilon(\%) = \left[-\left(\frac{d \ln I}{du} \times 0.9506 \right) - 1 \right] 100$	$20 \leq u \leq 60$
Van-Krevelen	$\varepsilon(\%) = \left[-\left(\frac{d \ln I}{du} \right) - \frac{1}{u} - 1 \right] 100$	-
Horowitz-Metzger	$\varepsilon(\%) = \left[-\left(\frac{d \ln I}{du} \right) - 1 \right] 100$	-
Gyulai-Greenhow	$\varepsilon(\%) = \left[\left[-\left(\frac{d \ln I}{du} \right) \left(\frac{E^{0.04177}}{621.302R} \right) \right]^{1.04359} - 1 \right] 100$	$20 \leq u \leq 60$
MacCallum-Tanner	$\varepsilon(\%) = \left[\left[-\left(\frac{d \ln I}{du} \right) - \left(\frac{1034.56R}{E} \right) \right] \left(\frac{0.002}{R} \right) - 1 \right] 100$	-

Table 3. Values of the relative error (percentage ε) for the approximation calculated by means of the different equations as a function of the parameter u .

u	Coats-Redfern	Doyle	Van-Krevelen	Horowitz-Metzger
2	-19.72	71.37	30.28	80.28
5	-4.76	28.56	15.23	35.23
10	-1.47	12.67	8.53	18.53
15	-0.71	7.06	5.95	12.62
20	-0.42	4.17	4.58	9.58
30	-0.20	1.21	3.13	6.47
40	-0.11	-0.29	2.39	4.89
50	-0.07	-1.20	1.92	3.92
60	-0.05	-1.82	1.61	3.28
80	-0.03	-2.59	1.22	2.47
100	-0.02	-3.06	0.98	1.98

included in Table 3 point out that the activation energy can be determined from the Coats-Redfern method with accuracy better than 5% even for u values lower than 5. This fact seems to indicate that this method can be used for performing the kinetic analysis in a range of u larger than that proposed by the authors [16]. A comparison of the data included in Table 3 with those listed in Tables 4 and 5 points out that the method of MacCallum-

Tanner leads to errors higher than those obtained using the other procedures investigated here.

EXPERIMENTAL

Materials

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee,

Table 4. Values of the relative error (percentage ϵ) for the approximation calculated by means of the Gyulai-Greenhow equation as a function of the parameters u and T .

T (K)	$u = E/RT$										
	2	5	10	15	20	30	40	50	60	80	100
300	49.38	15.17	3.44	-0.18	-1.77	-2.98	-3.28	-3.26	-3.13	-2.71	-2.25
400	51.26	16.63	4.75	1.07	-0.53	-1.75	-2.05	-2.04	-1.91	-1.48	-1.01
500	52.74	17.77	5.77	2.06	0.44	-0.79	-1.10	-1.08	-0.95	-0.52	-0.05
600	53.96	18.71	6.62	2.88	1.24	0.00	-0.31	-0.29	-0.16	0.28	0.75
700	55.00	19.51	7.33	3.57	1.92	0.67	0.36	0.38	0.52	0.95	1.43
800	55.90	20.20	7.96	4.18	2.52	1.26	0.95	0.96	1.10	1.54	2.02
900	56.71	20.82	8.52	4.72	3.05	1.78	1.47	1.48	1.62	2.06	2.55
1000	57.43	21.38	9.02	5.19	3.52	2.25	1.94	1.95	2.09	2.53	3.02
1100	58.08	21.88	9.47	5.63	3.95	2.67	2.36	2.37	2.52	2.96	3.44

Table 5. Values of the relative error (percentage ϵ) for the approximation calculated by means of the MacCallum-Tanner equation as a function of the parameters u and T .

T (K)	$u = E/RT$										
	2	5	10	15	20	30	40	50	60	80	100
300	-92.11	-33.40	-15.53	-9.92	-7.20	-4.55	-3.25	-2.48	-1.98	-1.35	-0.97
400	-48.78	-16.07	-6.87	-4.14	-2.87	-1.66	-1.08	-0.75	-0.53	-0.26	-0.11
500	-22.79	-5.07	-1.67	-0.68	-0.27	0.07	0.22	0.29	0.33	0.38	0.41
600	-5.46	1.26	1.80	1.63	1.47	1.23	1.08	0.99	0.91	0.82	0.76
700	6.92	6.21	4.27	3.28	2.70	2.05	1.70	1.48	1.32	1.13	1.01
800	16.20	9.93	6.13	4.52	3.63	2.67	2.17	1.85	1.63	1.36	1.19
900	23.42	12.81	7.57	5.48	4.35	3.15	2.53	2.14	1.87	1.54	1.34
1000	29.20	15.12	8.73	6.25	4.93	3.54	2.82	2.37	2.07	1.68	1.45
1100	33.92	17.02	9.67	6.88	5.41	3.85	3.05	2.56	2.22	1.80	1.55

WI, USA), and Riedel-de Haen AG (Seelze, Germany). *N,N*-Dimethylacetamide (DMAc) (Merck, Darmstadt, Germany), *N,N*-dimethylformamide (DMF) Riedel-de Haen AG (Seelze, Germany), 1-methyl-2-pyrrolidone (NMP) (Merck, Darmstadt, Germany) and pyridine (Py) (Merck, Darmstadt, Germany) were dried over BaO and then were distilled under reduced pressure. 1,4-Diazobicyclo[2.2.2]octane (DABCO) was purchased from Merck (Darmstadt, Germany) and used without further purification.

Equipment

Proton nuclear magnetic resonance ^1H NMR (500 MHz) spectra were recorded in DMSO- d_6

solution using a Bruker (Ettlingen, Germany) Avance 500 instrument. FTIR spectra were recorded on Jasco-680, (Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wavenumbers (cm^{-1}). Inherent viscosities were measured using a Cannon Fenske Routine Viscometer (Cannon, Mainz, Germany) at a concentration of 0.5 g.dL^{-1} at 25 cm^{-1} . Specific rotations were measured by a Jasco P-1030 Polarimeter (Toyonaka, Osaka, Japan). All melting points were taken with a (Gallenkamp, England) melting point apparatus. Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. Elemental analyses were determined with an Elementar

Analysensysteme GmbH VarioEL in CHNS mode by Iran Polymer and Petrochemical Research Institute (IPPI), Tehran, Iran. Thermogravimetric analysis (TGA) data for polymers were taken on a Perkin Elmer (Karlsruhe, Germany) at a heating rate of 10°C/min under nitrogen atmosphere by IPPI. Differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument (London, UK) at a heating rate of 20°C/min under nitrogen atmosphere by IPPI. Glass transition temperatures (T_g) were recorded at the middle of the transition in the heat capacity taken from the heating DSC traces.

Monomer Synthesis

5-[3-Methyl-2-(1,8-naphthalimidyl)butanoylamino]isophthalic acid (1) was prepared according to our previous work [41].

Polymer Synthesis

Polymerization of Diacid 1 with Diisocyanates 2-5 in NMP Under Gradual Heating

The following procedures were applied to all polymerizations. In a 25-mL round-bottomed flask 4,4'-methylenebis(phenylisocyanate) MDI (2) (0.05 g , $2.17 \times 10^{-4} \text{ mol}$) was added to a solution of diacid (1) (0.10 g , $2.17 \times 10^{-4} \text{ mol}$) in 0.18 mL of NMP. The mixture was stirred at room temperature (RT) and then triethylamine (TEA) (0.02 g , $2.78 \times 10^{-5} \text{ mol}$) was added. The solution was stirred for 1 h at RT and further 1 h at 60°C. Then, it was gradually heated from 60°C to 90°C for 4 h, with another 2 h at 100°C, and finally one more hour at 120°C. During this period, 0.2 mL of NMP was added. The reaction mixture was poured into 10 mL of methanol to precipitate the polymer. The solid was filtered off, dried to give 0.12 g (83%) of yellow solid PA3. This polymerization was also repeated using Py, dibutyltin dilaurate (DBTDL), tributylamine (TBA) and DABCO as catalysts, and without any catalyst, respectively. The reaction proceeded efficiently in the presence of the above catalyst. The optimized reaction conditions according to reaction time and reaction catalysts were selected for the polymerization of diacid monomer 1 with other diisocyanates such as toluene-2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI).

Polymer PA1: FTIR (KBr, cm^{-1}): 3314 (w), 3109 (w), 2953 (w), 1706 (m), 1668 (s), 1590 (s), 1509 (s), 1430 (m), 1413 (m), 1376 (m), 1340 (m), 1310 (m), 1238 (m), 1200 (w), 1103 (w), 1018 (w), 909 (w), 845 (w), 781 (w), 754 (w). $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.73 (d, 3H, CH_3 , $J = 5.05 \text{ Hz}$), 1.24 (d, 3H, CH_3 , $J = 4.90 \text{ Hz}$), 2.84 (m, 1H, CH), 3.87 (s, 2H, CH_2), 5.31 (d, 1H, CH, $J = 8.35 \text{ Hz}$), 7.19 (d, 2H, CH, $J = 7.20 \text{ Hz}$), 7.66 (d, 2H, CH, $J = 7.40 \text{ Hz}$), 7.91 (s, 2H, CH), 8.14 (s, 1H, CH), 8.26 (s, 2H, CH), 8.54 (dd, 2H, CH, $J_1 = 16.05 \text{ Hz}$, $J_2 = 6.60 \text{ Hz}$), 9.95 (s, 1H, NH), 10.35 (s, 1H, NH).

Polymer PA4: FTIR (KBr, cm^{-1}): 3311 (s), 3116 (w), 2928 (s), 2853 (s), 1711 (s), 1663 (s), 1654 (s), 1587 (m), 1561 (s), 1432 (w), 1376 (m), 1345 (w), 1269 (w), 1244 (m), 1187 (w), 1130 (w), 1106 (w), 1024 (w), 905 (m), 842 (w), 778 (s), 746 (w), elemental analysis calculated for $(\text{C}_{32}\text{H}_{26}\text{N}_4\text{O}_5)_n$ (546.57 g/mol)_n: C, 70.32%; H, 4.79%; N, 10.25%; Found: C, 70.12%; H, 5.00%; N, 10.12%.

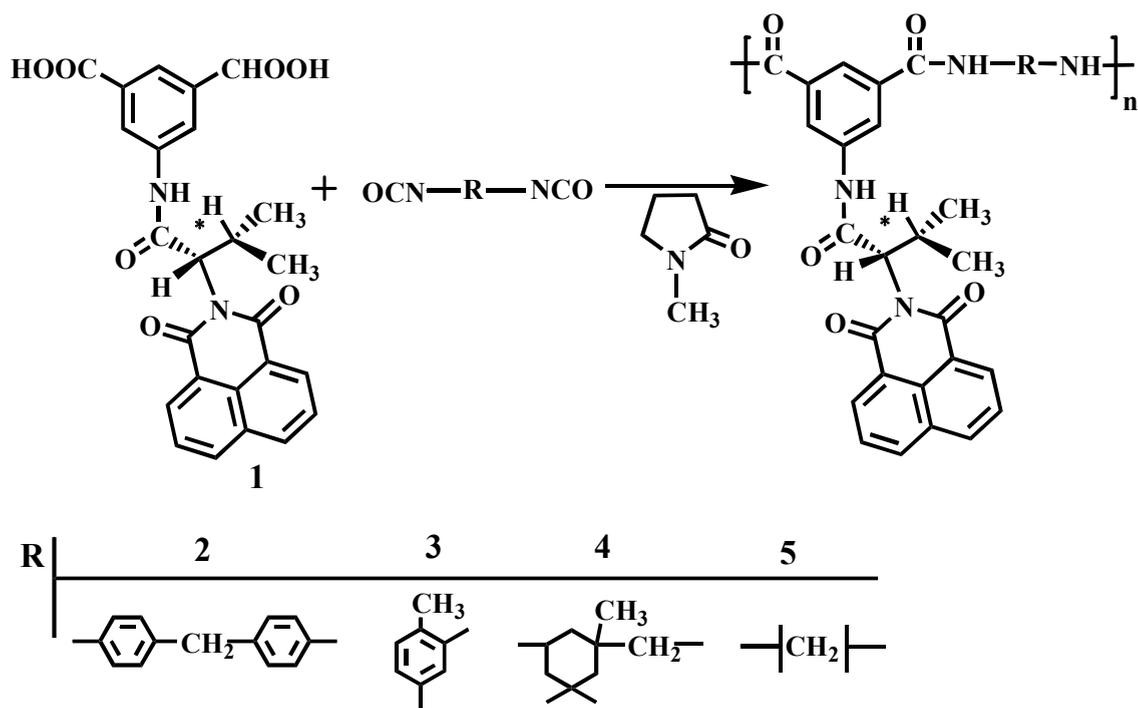
Polymer PA7: FTIR (KBr, cm^{-1}): 3317 (m), 3076 (m), 2949 (m), 2927 (s), 2851 (s), 1706 (m), 1667 (s), 1587 (s), 1553 (s), 1432 (s), 1377 (m), 1343 (m), 1286 (w), 1239 (w), 1188 (w), 1153 (w), 1116 (m), 1072 (m), 1027 (w), 909 (s), 842 (s), 780 (m), 745 (s), 712 (s), elemental analysis calculated for $(\text{C}_{35}\text{H}_{37}\text{N}_4\text{O}_5)_n$ (593.69 g/mol)_n: C, 70.81%; H, 6.28%; N, 9.44%; Found: C, 70.58%; H, 6.42%; N, 9.30%.

Polymer PA11: FTIR (KBr, cm^{-1}): 3305 (s), 3074 (w), 2924 (s), 2860 (s), 1707 (s), 1665 (s), 1633 (s), 1588 (w), 1541 (s), 1466 (w), 1436 (m), 1373 (m), 1341 (m), 12736 (w), 1239 (m), 1185 (w), 1110 (w), 1028 (w), 938 (w), 909 (w), 844 (w), 779 (m), 744 (w). $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 0.71 (d, 3H, CH_3 , $J = 5.17 \text{ Hz}$), 1.23 (d, 3H, CH_3 , $J = 5.59 \text{ Hz}$), 1.22-1.31 (m, 12H, CH_2), 2.82 (m, 1H, CH, $J = 6.40 \text{ Hz}$), 5.27 (d, 1H, CH, $J = 8.06 \text{ Hz}$), 8.00 (s, 2H, CH), 8.11 (s, 1H, CH), 8.41 (s, 2H, CH), 8.57 (t, 4H, CH, $J = 11.18 \text{ Hz}$), 9.77 (s, 2H, NH), 9.85 (s, 1H, NH).

RESULTS AND DISCUSSION

Polymer Synthesis

Polycondensation reaction of a dicarboxylic acid with different aromatic and aliphatic diisocyanates using different catalysts to form amide bonds is an efficient



Scheme I. Polycondensation reactions of monomer 1 with different diisocyanates.

way to obtain polyamides of moderate to high degree of polymerization on a laboratory scale. This method was successfully applied for the preparation of PAs (1-12) from dicarboxylic acid 1 with various diisocyanates (2-5) (Scheme I) and the results are shown in Table 6.

Thermal Properties

The thermal properties of PA1, PA4, PA7 and PA11 were evaluated by means of TGA/DTG and DSC in a nitrogen atmosphere at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. All the PAs exhibited good resistance to thermal decomposition up to 300°C in nitrogen and began to

Table 6. Reaction conditions for the polymerization of diacid 1 with different diisocyanates and some physical properties of PA1-PA12.

Polymer	Diisocyanate	Catalyst	Non-solvent	Yield (%)	η_{inh}^a (dL/g)	$[\alpha]_{\text{Na},589}^{25,b}$
PA1	MDI	DBTDL	MeOH/Water	86	0.54	-62.0
PA2	MDI	No cat	MeOH/Water	72	0.35	-47.0
PA3	MDI	TEA	MeOH/Water	83	0.56	-53.5
PA4	HDI	DBTDL	MeOH/Water	86	0.36	-32.4
PA5	HDI	No cat	MeOH/Water	87	0.34	-35.2
PA6	HDI	TEA	MeOH/Water	82	0.31	-37.2
PA7	IPDI	DBTDL	Water	87	0.27	-42.0
PA8	IPDI	No cat	Water	81	0.21	-39.1
PA9	IPDI	TEA	Water	81	0.24	-47.2
PA10	TDI	DBTDL	Water	83	0.35	-41.0
PA11	TDI	No cat	Water	74	0.32	-43.1
PA12	TDI	TEA	Water	83	0.35	-47.0

^(a) Measured at a concentration of 0.5 g/dL in DMF at 25°C ; ^(b) Measured under the conditions as in inherent viscosity.

Table 7. Thermal properties of PA1, PA4, PA7 and PA11.

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char yield ^c	T _g (°C) ^d	DTG	LOI ^e
PA1	395	431	46	193	421	36
PA4	324	360	49	151	342	37
PA7	341	374	44	134	360	35
PA11	409	440	52	147	429	38

(a) Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere;

(b) Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10°C/min in a nitrogen atmosphere;

(c) Percentage weight of material left undecomposed after TGA analysis at a temperature of 800°C in a nitrogen atmosphere; (d) Glass transition temperature was recorded at a heating rate of 20°C/min in a nitrogen atmosphere;

(e) Limiting oxygen index (LOI) evaluating at char yield of 800°C.

decompose gradually above that temperature. Several thermal regions were selected on the TGA curves for comparison of the relative thermal stabilities of PAs. The thermoanalyses data of these polymers are summarized in Table 7. The temperature of 10% weight loss for resulting polymers was higher than 360°C and the amount of residue (char yield) of these polymers in a nitrogen atmosphere was more than 44% at 800°C. DSC of PAs was also run, and its T_g was about 134-193°C. The data listed in Table 7 reveal that T_gs of these polymers are not very high, yet they are high in comparison with those of traditional aliphatic poly(amide-imide)s and aliphatic PAs. T_g value for the polymer prepared from diisocyanate 2 was higher than those from 3, 4 and 5. The T_g values generally decreased with the decreasing order of segmental flexibility of the diisocyanate moiety. Char yield can be applied as criteria for estimated limiting oxygen index (LOI) of the polymers in accordance with Van-Krevelen and Hoftzyer equation [42]. LOI = 17.5 + 0.4 CR where CR = char yield. The polymers had LOI values calculated from their char yield was higher than 35. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers.

Checking the Errors with Simulated and Experimental Curves

In order to check the above conclusions we have used the approximation of five theoretical curves shown in Figure 1, that has been simulated by assuming an F1 kinetic model (unimolecular decay law) [Table 8, e.g., $g(\alpha) = -\ln(1-\alpha)$], for linear heating rate $\beta = 10^\circ\text{C}/\text{min}$ and a range of values of the activation energy and the preexponential factor selected in such a way as to

cover a wide range of u and T values. These curves have been computed by numerical integration of eqn (3) by the Runge-Kutta's procedure using the Mathcad software with a precision of 10⁹%. The values of activation energies and error obtained from this analysis are shown in Table 9 and included in Figure 1. The resulting values of error percentage (ϵ) are consistent with those tabulated in Tables 3-5. However, the small deviations observed in this process are due to determination of u values. On the other hand, the values of T vary during the experimental process therefore, the values of u would not be constant during the entire simulated curve. Figure 2 shows the thermal decompositions of the PA1, PA4, PA7 and PA11 which have been analyzed

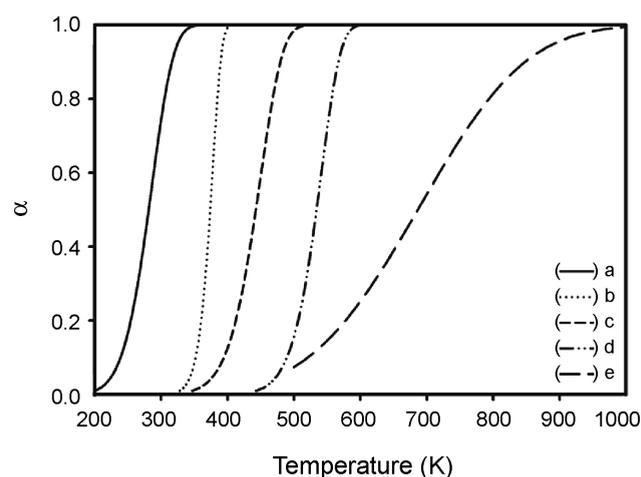


Figure 1. Simulated curves by assuming a random nucleation mechanism (F1), a heating rate $\beta = 10^\circ\text{C}/\text{min}$ and the following kinetic parameters: (curve a): $E = 5 \text{ kcal/mol}$, $A = 2000 \text{ min}^{-1}$, (curve b): $E = 21 \text{ kcal/mol}$, $A = 10^{12}$, (curve c): $E = 12 \text{ kcal/mol}$, $A = 2 \times 10^5 \text{ min}^{-1}$, (curve d): $E = 20 \text{ kcal/mol}$, $A = 4 \times 10^7$, and (curve e): $E = 6 \text{ kcal/mol}$, $A = 5 \text{ min}^{-1}$.

Table 8. List of reaction models typically used in kinetic analyses [5-14].

Symbol	Mechanisms	Integral form, $g(\alpha)$	Differential form, $f(\alpha)$
Random nucleation and nuclei growth, Avrami-Erofev equation			
A2	Bidimensional nuclei growth	$[-\ln(1-\alpha)]^{1/2}$	$2[-\ln(1-\alpha)]^{1/2} (1-\alpha)$
A3	Three-dimensional nuclei growth	$[-\ln(1-\alpha)]^{1/3}$	$3[-\ln(1-\alpha)]^{2/3} (1-\alpha)$
Random nucleation and nuclei growth			
F1	First order random nucleation	$[-\ln(1-\alpha)]$	$(1-\alpha)$
Diffusion			
D1	One-dimensional diffusion	α^2	$1/(2\alpha)$
D2	Two-dimensional diffusion	$(1-\alpha) \ln(1-\alpha) + \alpha$	$1/[\ln(1-\alpha)]$
Limiting surface reaction between both phases			
R2	Cylindrical symmetry	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
R3	Spherical symmetry	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$

Table 9. Values of the activation energies (E_a) and errors (ϵ percentage) obtained of the analysis of the simulated curves by means of different integral methods.

Method	Curve A		Curve B		Curve C		Curve D		Curve E	
	E_a^b	ϵ (%)								
Coats-Redfern	4.92	-1.6	20.95	-0.2	11.92	-0.7	19.91	-0.4	5.69	-5.2
Doyle	5.78	15.6	21.33	1.57	13.01	8.4	20.97	4.8	7.98	33.0
Van-Krevelen	5.56	11.2	21.74	3.5	12.88	7.3	21.05	5.2	7.09	18.2
Horowitz-Metzger	6.18	23.6	22.50	7.1	13.81	15.1	22.13	10.6	8.48	41.3
Gyulai-Greenhow	5.27	5.4	20.59	2.8	12.30	2.5	20.23	1.1	7.38	23.0
MacCallum-Tanner	4.04	-19.2	20.48	2.3	11.69	-2.6	20.10	0.5	6.37	6.2

(b) The activation energy (kcal/mol).

by means of the differential and integral methods by assuming an F1 kinetic model. For the integral analysis, the six different approaches which have been mentioned before were used in this study. Table 10 includes the resulting values of the activation energy, correlation coefficient and errors in the activation energy, as calculated by assuming the value of E obtained from the differential method as the correct one because no approximation is used for deriving eqn (1). Using the kinetic parameter obtained from the differential method, the PAs

decomposition curve has been reconstructed under heating rate condition ($\beta = 10^\circ\text{C}/\text{min}$) and the agreement between the experimental and simulated curves was excellent (these results have not been shown in the present article). It was found that the E_a values obtained from different approaches slightly differ from each other. The approximation of Coats-Redfern is the one that leads to the smallest errors in the determination of the activation energy, followed by that of Doyle is the least accurate one in terms of determining activation energies.

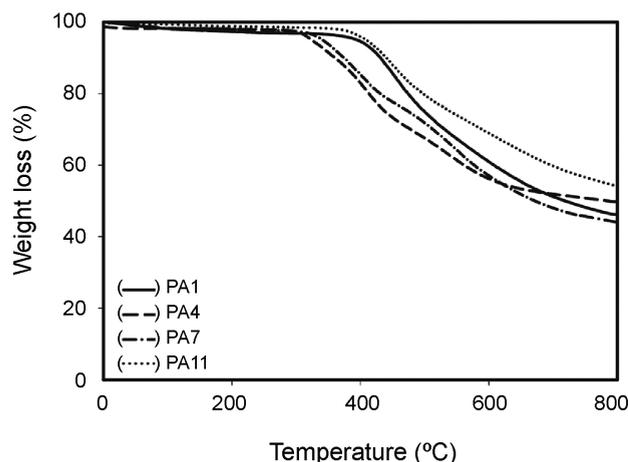


Figure 2. Experimental TGA curves for PA1, PA4, PA7 and PA11, at heating rate of 10°C/min.

Accordingly, for the decomposition stage in all cases by plotting the left-hand side of eqn (3) as a function of $-1/T$ (Figure 3) E was calculated from the slope and A was calculated from the intercept value as described in an earlier work [4-12]. ΔS was calculated using the following equation (eqn (23)):

$$\Delta S = 2.303 R \log(Ah/kT_M) \quad (23)$$

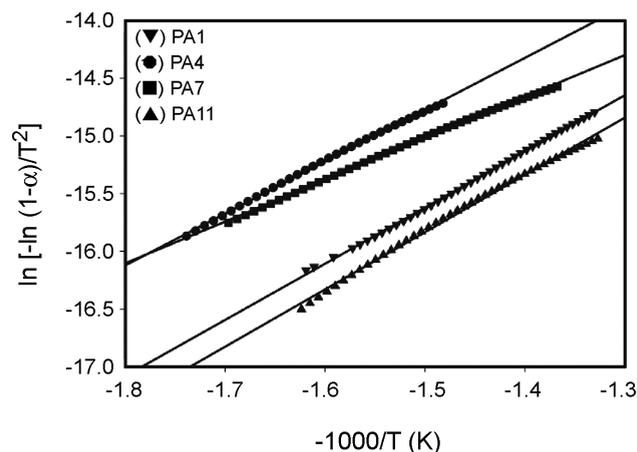


Figure 3. A typical plot of $\ln[-\ln(1-\alpha)/T^2]$ against $-1000/T$ for PA1, PA4, PA7 and PA11.

where h and k are the Planck and Boltzmann constants, respectively, and T_M is the peak temperature from the DTG curve. As the reaction rate depends mainly on the free energy of activation, the entropy of activation ΔS should decide the magnitude of ΔG according to $\Delta G = E - T\Delta S$. The enthalpy of activation was calculated using $E = \Delta H + RT_M$. Hence $\Delta H = E - RT_M$. The kinetic parameters for the

Table 10. Results of the kinetic analysis of the thermal decomposition curve for the PA1, PA4, PA7 and PA11 by different methods.

Method		Differential	Coats-Redfern	Doyle	Van-Krevelen	Horowitz-Metzger	Gyulai-Greenhow	MacCallum-Tanner
PA1	E_a^b	9.890	9.69	11.79	11.06	12.40	11.09	10.39
	ε (%)	-	-2.00	19.20	11.80	25.40	12.1	5.00
	r	0.999	0.999	0.999	0.999	0.999	0.999	0.999
PA4	E_a^b	7.310	7.19	9.30	8.52	9.88	8.66	7.77
	ε (%)	-	-1.60	27.20	16.60	35.20	18.5	6.30
	r	0.998	0.999	0.999	0.998	0.994	0.999	0.999
PA7	E_a^b	9.080	8.95	10.85	10.20	11.42	10.17	9.40
	ε (%)	-	-1.40	19.50	12.30	25.80	12.0	3.50
	r	0.998	0.999	0.999	0.998	0.996	0.999	0.999
PA11	E_a^b	10.10	9.86	11.95	11.26	12.59	11.25	10.57
	ε (%)	-	-2.40	18.30	11.50	24.60	11.4	4.60
	r	0.999	0.997	0.999	0.996	0.993	0.999	0.999

(b) The activation energy (kcal/mol).

Table 11. Kinetic parameters for the degradation of PAs determined using the Coats-Redfern.

Polymer	Parameter					r
	E_a (kcalmol ⁻¹)	A (s ⁻¹)	ΔS (kcalmol ⁻¹ K ⁻¹)	ΔH (kcalmol ⁻¹)	ΔG (kcalmol ⁻¹)	
PA1 (342-482)	9.86	0.19	-0.06	8.50	52.08	0.997
PA4 (300-424)	8.95	0.24	-0.06	7.70	47.01	0.999
PA7 (305-459)	7.19	0.04	-0.07	5.87	49.81	0.999
PA11 (342-480)	9.69	0.20	-0.07	8.32	51.82	0.999

non-isothermal decomposition and the temperature range in which each decomposition step occurs are summarized in Table 11. The positive values of ΔH indicate that the dissociation processes are endothermic and enhanced with the rise of temperature. ΔG values for the dissociation constants are positive, thus dissociation processes are non-spontaneous. A positive value of ΔS indicates a malleable activated compound that leads to a large number of degrees of freedom of rotation and vibration. On the other hand, a negative value of ΔS is an indication of a highly ordered activated complex and the degrees of freedom of rotation as well as of vibration are less than they in the non-activated complex [43-45].

CONCLUSION

Direct polymerization reaction of monomer 1 with various diisocyanates furnished new optically active PAs containing S-valine amino acid moiety. The main advantage of this polycondensation reaction is that, in this procedure we do not need to prepare diacid chloride, therefore time and energy are being saved. More important, in this investigation it has been shown that, for a kinetic analysis using the various analytical methods revealed that, there are tremendous variations depending upon the mathematical approach taken in the analysis. Because of the wide variations in the kinetic parameters obtained within the extraction of the kinetic triplet, activation energy, frequency factor and kinetic model from the decomposition data, different approximations of the temperature integral are used for various integral methods. Furthermore, a new

classification approach was proposed to divide the integral methods into two types, in terms of their different ways to treat the temperature integral. The two types of integral methods and their adopted temperature integral approximations are analyzed in details. The error analysis of activation energy shows that the Coats-Redfern method can lead to more accurate value of frequency factor than others. Comparatively, the MacCallum-Tanner method has higher error of activation energy and produces great error of the frequency factor, and thus it is not recommended to be used in kinetic analysis. The thermal stability and non-isothermal degradation data of the activation energies, the entropy of activation, free energy of activation and enthalpy of activation for optically active PA1, PA4, PA7 and PA11 were also calculated using the Coats-Redfern method. Additionally, the error in the activation energy obtained from the methods of Van-Krevelen and Horowitz-Metzger would be influenced by the value of the reference temperature. The values of the errors have been checked by analyzing the simulated and experimental curves via different methods, showing an excellent agreement.

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