Kinetics and Thermal Degradation Study of Optically Active and Thermally Stable Aromatic Polyamides with Flame-Retardancy Properties

By Shadpour MALLAKPOUR* and Mehdi TAGHAVI

Aromatic diacid monomer containing L-phenylalaninetetrabromophthalimide group was synthesized in three steps in high yield and purity. Several, highly soluble and optically active aromatic polyamides (PA)s with flame-retardancy properties were prepared from this diacid monomer and different aromatic diamines under microwave irradiation as well as conventional heating. Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) for these PAs have been extensively used for thermal decomposition study in order to determine the actual reaction mechanism, half-life time and lifetime of the decomposition process. Non-isothermal integral methods, differential method and Criado method were utilized to obtain the kinetic parameters (E , ΔS , ΔG , ΔH and reaction mechanism) from TGA and DTG curves. All of the synthesized compounds and some representative PAs were characterized by ^1H NMR, FT/IR, elemental analysis and specific rotation techniques.

KEY WORDS: Thermally Stable Polyamides / Kinetic Study / Optically Active Polymers / Microwave Irradiation / Flame Retardant Polymer / Mechanism of Solid State Reaction / Green Chemistry /

Studies of thermal degradation of polymers have great interest for determining the thermal stability and characterization of polymer materials, as well as it contributes to the solution of environmental problems. In polymer science, thermal methods of analysis have found important applications, among them the determination of kinetic parameters. For this purpose, thermogravimetry (TG) and differential scanning calorimetry (DSC) because of its simplicity have been widely used in polymer science to study the kinetics and mechanism of solid thermal decomposition reactions, generally carried out under a linear temperature program.^{1–5} The simplest experiment to determine the kinetics of a thermal decomposition is TG under non-isothermal conditions. Kinetic parameters such as activation energies and pre-exponential factors are calculated using integral and differential methods reported in the literature. Knowledge of kinetic parameters can be obtained through various TG data treating methods. With proper experimental procedures, information about the kinetics of decomposition and in-use lifetime projections can be obtained. In many polymer applications, the ability to predict product lifetime is valuable because the costs of premature failure in actual end use can be high.^{6–8}

The synthesis and properties of chiral polymers is of particular interest from the viewpoint of material science. Most of the natural polymers such as polysaccharides and proteins are optically active. Amino acids are among the simplest biomolecules that contain intramolecular hydrogen bonds and proteins. Amino acid based synthetic polymers are also expected to show biodegradability and biocompatibility similar to those of polypeptides. An effective and direct way for

synthesizing chiral polymers is to introduce chiral elements into the polymer backbone or the side chains. Among the synthetic polyamides (PA)s, 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. These applications have created more effort to improve different synthetic procedures of optically active polymers. Up to now, chiral polymers have found successful uses in chiral chromatographic separations and shown potential applications in optical switches, liquid crystals, chiral catalytic systems and biomedical devices.^{9–11} Among many polymer systems, aromatic PAs possess many desirable characteristics, such as thermal stability, chemical resistance, and low flammability, along with excellent mechanical properties.^{12–15} However, most of them have traditionally been difficult to process by spin coating because of their high glass-transition temperatures and poor solubility in organic solvents, which limit their widespread applications. Therefore, numerous efforts have been made to improve their processability by structural modification. The incorporation of pendent bulky, packing-disruptive groups along the polymer backbone outcomes in a less ordered polymer matrix, hence increasing the solubility characteristics, while other advantageous properties are retained.^{16–19}

The improvement of the fire behavior and thermal stability of polymer is today the aim of numerous studies. The research and development of flame retardant polymeric materials always receives great attention whether in fundamental research or industry exploitation. This has led to efforts of finding ways to modify ignition, flame spread, heat production as well as

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, I.R. Iran

*To whom correspondence should be addressed (Tel: +98-311-391-3267, Fax: +98-311-391-2350, E-mail: mallak@cc.iut.ac.ir, mallak777@yahoo.com (Shadpour Mallakpour)).

Table I. Algebraic expressions for $g(\alpha)$ and $f(\alpha)$ for the most frequently used mechanisms of solid state processes [3–6]

Symbol	Mechanisms	Integral form, $g(\alpha)$	Differential form, $f(\alpha)$
Random nucleation and nuclei growth			
F1	Random nucleation with one nucleus on the individual particle	$[-\ln(1 - \alpha)]$	$(1 - \alpha)$
F2	Random nucleation with two nuclei on the individual particle	$[\alpha/(1 - \alpha)]$	$(1 - \alpha)^2$
Diffusion			
D1	One-dimensional diffusion	α^2	$1/(2\alpha)$
D2	Two-dimensional diffusion	$(1 - \alpha) \ln(1 - \alpha) + \alpha$	$1/[\ln(1 - \alpha)]$
Random nucleation and nuclei growth, Avrami-Erofev equation			
A2	Nucleation and growth: Avrami eq (1)	$[-\ln(1 - \alpha)]^{1/2}$	$2[-\ln(1 - \alpha)]^{1/2}(1 - \alpha)$
A3	Nucleation and growth: Avrami eq (2)	$[-\ln(1 - \alpha)]^{1/3}$	$3[-\ln(1 - \alpha)]^{2/3}(1 - \alpha)$
Limiting surface reaction between both phases			
R2	Phase boundary controlled reaction: contraction area	$[1 - (1 - \alpha)^{1/2}]$	$2(1 - \alpha)^{1/2}$
R3	Phase boundary controlled reaction: contraction volume	$[1 - (1 - \alpha)^{1/3}]$	$3(1 - \alpha)^{2/3}$

smoke, toxic and corrosive gases production.²⁰ The halogen-containing organic and polymeric materials especially, PAs and polyesters most commonly used as flame retardants in the plastic industry. The main advantage of polymeric flame retardants is that they are less volatile and less migratory, allowing high processor temperatures and application temperatures. Compounds containing the elements such as Br, Cl, P, N and Sb in general can promote a flame-retardancy effect of polymeric materials.²¹ The interest in bromine containing monomers has been directed towards the synthesis of polymers with reduced flammability. The world market for brominated flame retardants (BFR)s is increasing. Until the year 2000 the market of the BFRs in total is forecast to grow by 8% per year.²²

This article describes the successful synthesis and characterization of dicarboxylic acid containing pendant alkyltetrabromophthalimide groups and their use for the preparation of PAs by direct polycondensation with various aromatic diamines. The introduction of these side chiral chains should disrupt interchain hydrogen bonding and reduce packing efficiency and crystallinity. Moreover the presence of heat-resistant tetrabromophthalimide heterorings as pendant groups may counterbalance any loss of thermal properties that can be caused by the incorporation of aliphatic spacers. Therefore, this methodology should enhance solubility and maintain reasonably high glass transition temperature through controlled segmental mobility. Furthermore, we will focus on the thermal stability and thermal kinetic studies of the degradation process, in order to determine the activation energies, the mechanism of a solid-state process, half-life time and lifetime of resulting PAs were evaluated by using TG data.

Kinetic Study. The basic assumption of the thermal kinetics is that the Arrhenius equation representative of the reaction rate dependence of the temperature can be applied in the thermal analysis reaction, *i.e.*, for a simple reaction $aA_{(s)} \rightarrow bB_{(s)} + cC_{(g)}$, its reaction rate $d\alpha/dt$ can be written as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $f(\alpha)$ depends on the particular decomposition mechanism. The Arrhenius equation has the following formula:

$$k(T) = Ae^{-E/RT} \quad (2)$$

where A, the pre-exponential factor, is assumed to be independent of temperature, E is the activation energy, T the absolute temperature, and R the gas constant. The combination of eqs (1) with (2) gives the following relationship:

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \quad (3)$$

If the sample temperature is changed by a controlled and constant heating rate, $\beta = dT/dt$; the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the reaction rate may be written as follows:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \beta \frac{d\alpha}{dT} \quad (4)$$

The combination of eqs (3) and (4) gives the following expression:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (5)$$

Integration of the both sides of above equation and rearrangement give

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT \quad (6)$$

where $g(\alpha)$ is the integral function of conversion degree α . As far as the polymer is concerned, its degradation process, generally, obeys the sigmoidal or deceleration functions. For the different solid reaction mechanism, $g(\alpha)$ has different expressions (Table I).^{23–25} These expressions can be used to predict the solid reaction mechanism reflected by the dynamic TG curves. Based on the differential eq (5) and the integral eq (6), different approximate expressions (Table I) were

proposed to fit the TG data. These approximate expressions are the basis of study on the thermal kinetics of the flame-retarded materials in this paper.

Coats-Redfern Method (Integral Methods). After taking the integral approximation and logarithm of eq (16), following equations can be obtained:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - (E/RT) \quad \text{for } n \neq 1 \quad (7)$$

and

$$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) - (E/RT) \quad \text{for } n = 1 \quad (8)$$

Thus plot of

$$Y = \ln \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] \text{ vs. } \frac{1}{T} \quad \text{for } n \neq 1 \quad (9)$$

$$Y = \ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] \text{ vs. } \frac{1}{T} \quad \text{for } n = 1 \quad (10)$$

results in straight lines with slopes equal to $(-E/R)$ for the correct value of n , since it may be shown that, for most values of E and for the temperature range over which reactions generally occur, the expression

$$\ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \quad (11)$$

is sensibly constant. In that case, eqs (8) and (9) can be written as $y = ax + b$:

$$a = -E/R; b = \ln \frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right); x = \frac{1}{T} \quad (12)$$

where E and A can be calculated from the slope and the intercept. By using the α values, a plot of left side of eqs (8) or (9) vs. $1/T$ should give straight lines for a correct value of n . In the evaluation of eq (8), the best value for n was searched in the range from 0 to 5 to get a straight line. The n value giving a straight line with a highest correlation coefficient was assumed to be the order of the overall pyrolysis and combustion reactions.¹⁻⁵

Van-Krevelen Method (Integral Methods). In the Van Krevelen method, a temperature T_m is where the rate is maximal and determined from the peak of the DTG curve. This method requires only the relative mass of the sample, as a function of reaction temperature to determine the activation energy of the reaction. The Van-Krevelen method adopts the following equation:

$$\ln[-\ln(1 - \alpha)] = \ln B + \left(\frac{E}{RT_m} + 1 \right) \ln T \quad \text{for } n = 1 \quad (13)$$

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)} \right] = \ln B + \left(\frac{E}{RT_m} + 1 \right) \ln T \quad \text{for } n \neq 1 \quad (14)$$

where

$$B = \frac{A}{\beta} \left(\frac{E}{RT_m} + 1 \right)^{-1} \left(\frac{0.368}{T_m} \right)^{\frac{E}{RT_m}} \quad (15)$$

Generally, the logarithmic term on the right part of the above equations is regarded as constant. Then, the determination of the reaction order n can be finished by linear fitting of the left part of above equations dependence of $\ln T$. The n value at the best correlation coefficient (r) obtained is the real reaction order, and the apparent activation energy E and pre-exponential factor A can be hereby calculated.²⁻⁵

Differential Methods. This technique involves taking the basic eq (5) in the logarithmic form and utilizing the rates of weight loss at different temperature. A limitation of the integral methods of kinetic analysis is that the temperature integral does not have an exact analytical solution for linear heating rate program.^{2,3,5} Because, no approximation is used for deriving eqs (5) and (16), thus, the activation energy and correlation coefficient, calculated by assuming the value of E obtained from the differential method as the correct one. The slope of the plot of $[\ln(d\alpha/dT)/f(\alpha)]$ vs. $(1/T)$ is connected with the real activation energy, E , through the following expression:

$$\ln \left[\frac{(d\alpha/dT)}{f(\alpha)} \right] = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (16)$$

Criado Method. The kinetic parameters (E , n and A) of the thermal decomposition reaction have been obtained by the non-isothermal analytical method. In order to find out the reaction mechanism, we have employed reference theoretical master curves. A master plot is a characteristic curve independent of the condition of the measurement, that must be accomplished whatever would be the thermal pathway followed for reaching a particular α - T -t point. If the value of the activation energy is known the kinetic model of the process can be found in the following way. Firstly, Criado *et al.* defined a type of $Z(\alpha)$ function

$$Z(\alpha) = \frac{(d\alpha/dt)}{\beta} \pi(x) T \quad (17)$$

where $x = E/RT$ and $\pi(x)$ is an approximate expression obtained by integration against temperature, which cannot be expressed by simple analysis formulas. Paterson proposed a reasonable relationship between $\pi(x)$ and $P(x)$:

$$\pi(x) = x e^x P(x) \quad (18)$$

Senum and Yang and Flynn³⁻⁶ proposed an approximate biquadratic rational expression of $P(x)$:

$$P(x) = \frac{e^{-x}}{x} \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (19)$$

when $x > 20$, eq (19) can give error less than $10^{-5}\%$, which is the basis for analyzing the TG data in this paper. Combining of eqs (4), (17), and (18), the following relationship should be obtained:

$$Z(\alpha) = f(\alpha)g(\alpha) \quad (20)$$

Scheme 1. Synthesis of monomer 7.

The combination of eqs (5) and (20) results in the following equation:

$$Z(\alpha) = g(\alpha) \frac{\beta}{A} \frac{d\alpha}{dT} e^{E/RT} \quad (21)$$

From eqs (4), (17), and (18), the following relationship can also be obtained:

$$Z(\alpha) = \frac{E}{R} \frac{d\alpha}{dT} e^{E/RT} P(x) \quad (22)$$

where, $x = E/RT$, $P(x)$ has the expression shown as eq (19), and $d\alpha/dT$ can be calculated from the related DTG curve. eq (21) was used to plot the master $Z(\alpha)$ - α curve of the different reaction mechanisms and eq (22) was used to plot the experimental $Z(\alpha)$ - α curve according to the TG data. The comparison of the master $Z(\alpha)$ - α curve with the experimental $Z(\alpha)$ - α curve can easily and accurately predict the reaction mechanism of the thermal degradation reaction.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) was dried over barium oxide, followed by fractional distillation. 5-Aminoisophthalic acid were recrystallized from a mixture of *N,N*-dimethylformamide (DMF)/water (v/v ratio 4:1) mixture. 1,5-Naphthalenediamine (8), and 4,4'-diaminodiphenylmethane (9) were purified by recrystallization from water. Benzidine (10) was purified by recrystallization from ethanol. 4,4'-Diaminodiphenylether (11), 2,5-diaminotoluene (12), 1,3-phenylenediamine (13), and 1,4-phenylenediamine (14) were purified by sublimation.

Equipments

Proton nuclear magnetic resonance (^1H NMR, 500 MHz)

spectra were recorded in $\text{DMSO}-d_6$ solution using a Bruker (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. Proton resonances are designated as singlet (s), doublet (d), quartet (q) and multiplet (m). FT/IR spectra were recorded on Jasco-680 spectrophotometer (Japan). The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s) and broad (br). The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900 W). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g/dL at 25 °C. Specific rotations were measured by a Jasco Polarimeter (Japan). Quantitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. Thermogravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a heating rate of 10 °C/min under N_2 atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Differential scanning calorimetric (DSC) data were recorded on a DSC-PL-1200 instrument under nitrogen atmosphere by IPPI. Glass-transition temperatures (T_g) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. Elemental analyses were also performed by IPPI.

Monomer Synthesis

5-[3-Phenyl-2-(tetrabromophthalimidyl)propanoylamino]isophthalic acid (7) was prepared (Scheme 1) according to our previous work.³¹

Polymer Synthesis

Method 1. Polymerization of diacid 7 with diamines 8-15 under conventional heating.

The PAs were prepared by the following general procedure: as an example for the preparation of PA6, into a 10 mL round-bottomed flask fitted with a water cooled condenser and a magnetic stirrer, was placed a mixture of 0.10 g (1.29×10^{-4} mol) of dicarboxylic acid 7, 14 mg (1.29×10^{-4} mol) of

Table II. ^1H NMR and elemental analysis data of compounds 4, 5 and 7

Compound	Spectra data	
4	^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 3.29 (dd, 1H, CH, $J_1 = 11.16$ Hz, $J_2 = 12.66$ Hz), 3.50 (dd, 1H, CH, $J_1 = 4.79$ Hz, $J_2 = 9.52$ Hz), 5.14 (dd, 1H, CH, $J_1 = 4.92$ Hz, $J_2 = 7.99$ Hz), 7.15 (m, 5H, CH, Ar-H), 13.10 (s, 1H, COOH) ppm.	^{13}C NMR (500 MHz, $\text{DMSO}-d_6$): δ 170.37 (C, COOH), 163.75 (C, C=O), 138.27 (C, Ar), 138.02 (C, Ar), 130.70 (C, Ar), 129.56 (CH, Ar), 129.25 (CH, Ar), 127.47 (CH, Ar), 121.90 (C, Ar), 54.66 (CH), 34.67 (CH_2) ppm.
5	^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 3.28 (dd, 1H, CH, $J_1 = 11.19$ Hz, $J_2 = 12.66$ Hz), 3.49 (dd, 1H, CH, $J_1 = 4.74$ Hz, $J_2 = 9.47$ Hz), 5.16 (dd, 1H, CH, $J_1 = 4.91$ Hz, $J_2 = 8.02$ Hz), 7.15 (m, 5H, CH, Ar-H) ppm.	^{13}C NMR (500 MHz, $\text{DMSO}-d_6$): δ 170.26 (C, COOH), 163.71 (C, C=O), 138.24 (C, Ar), 137.92 (C, Ar), 130.65 (C, Ar), 129.52 (CH, Ar), 129.21 (CH, Ar), 127.44 (CH, Ar), 121.91 (C, Ar), 54.55 (CH), 34.62 (CH_2) ppm.
7	^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 3.23 (dd, 1H, CH, $J_1 = 10.13$ Hz, $J_2 = 12.02$ Hz), 3.62 (dd, 1H, CH, $J_1 = 4.00$ Hz, $J_2 = 9.56$ Hz), 5.24 (dd, 1H, CH, $J_1 = 5.37$ Hz, $J_2 = 7.75$ Hz), 7.19 (m, 5H, CH, Ar-H), 8.19 (s, 1H, CH, Ar-H), 8.43 (s, 2H, CH, Ar-H), 10.26 (s, 1H, CH, NH), 13.10 (s, 1H, COOH) ppm.	^{13}C NMR (500 MHz, $\text{DMSO}-d_6$): δ 167.33 (C, C=O), 167.25 (C, COOH), 163.81 (C, C=O), 139.99 (C, Ar), 138.11 (C, Ar), 138.03 (C, Ar), 132.58 (C, Ar), 131.18 (C, Ar), 129.86 (CH, Ar), 129.24 (CH, Ar), 127.48 (CH, Ar), 125.96 (CH, Ar), 125.24 (CH, Ar), 121.70 (C, Ar), 56.17 (CH), 34.85 (CH_2) ppm.

diamine 13, 0.10 mL of triphenyl phosphite (TPP), 0.15 mL of pyridine (Py), 0.08 g of calcium chloride and 0.50 mL of NMP. The stirrer was operated and the mixture was refluxed for 5 h under nitrogen atmosphere. After cooling, the reaction mixture was poured into 30 mL of methanol with constant stirring. The precipitate was collected on a filter and washed thoroughly with methanol and hot water. The solid was dried under vacuum to give 0.09 g of PA6 (82% yield). The inherent viscosity of the resulting PA in DMF was 0.63 dL g^{-1} , measured at a concentration of 0.5 dL g^{-1} at 25°C .

Method II. Polymerization of diacid 7 with diamines 8-15 under microwave irradiation. The PAs were prepared by the following general procedure: as an example: for the preparation of PA10, a mixture of 0.10 g (1.29×10^{-4} mol) of diacid 7, 0.15 mL of Py, 0.10 mL of TPP, and 0.5 mL of NMP were placed in a porcelain dish and the mixture was ground completely for 5 min, then 0.08 g of calcium chloride and 26 mg (1.29×10^{-4} mol) of diamine 9 was added and the mixture was ground for 3 min. The reaction mixture was irradiated in the microwave oven for a period of $90 + 30$ s at 70% (630 W) of its power level. The resulting viscous solution was poured into 30 mL of methanol, filtered, dried under vacuum to give 0.11 g (88%) of PA10. The other PAs, PA9-PA16 were prepared using an analogous procedure.

PA3. FT/IR (KBr, cm^{-1}): 3365 (m), 3063 (m), 2960 (w), 1775 (w), 1721 (s), 1669 (s), 1593 (s), 1500 (s), 1445 (w), 1412 (m), 1383 (m), 1335 (m), 1240 (m), 1182 (w), 1156 (w), 1116 (m), 1004 (w), 970 (w), 890 (w), 821 (w), 749 (m), 700 (w). Elemental analysis calculated for $\text{C}_{37}\text{H}_{22}\text{Br}_4\text{N}_4\text{O}_5$ (922.21 g/mol): C, 48.19%; H, 2.40%; N, 6.08%. Found: C, 47.53%; H, 2.66%; N, 6.09%.

PA8. FT/IR (KBr, cm^{-1}): 3408 (m), 3061 (w), 2958 (w), 1774 (w), 1721 (s), 1669 (s), 1593 (m), 1513 (s), 1410 (s), 1384 (m), 1338 (m), 1243 (w), 1156 (w), 1115 (w), 1020 (w), 890 (w), 814 (w), 749 (w), 700 (w). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 3.22–3.35 (distorted dd, br, 1H, overlapped with H_2O , CH), 3.64 (dd, 1H, CH, $J_1 = 3.66$ Hz, $J_2 = 8.37$ Hz), 5.24 (dd, 1H, CH, $J_1 = 5.52$ Hz, $J_2 = 7.83$ Hz), 7.22 (m, 5H, CH), 7.97 (dd, 4H, CH, $J_1 = 9.16$ Hz, $J_2 = 18.11$ Hz), 8.26 (s, 1H, CH), 8.35 (s, 2H, CH), 10.34 (s, 1H, NH), 10.88 (s, 1H, NH) ppm.

PA10. FT/IR (KBr, cm^{-1}): 3408 (m), 3065 (w), 2923 (w), 1776 (w), 1722 (w), 1668 (m), 1593 (m), 1513 (s), 1410 (s), 1384 (m), 1338 (m), 1244 (w), 1157 (w), 1115 (w), 1020 (w), 891 (w), 749 (w), 700 (w). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 3.28–3.33 (distorted dd, br, 1H, overlapped with H_2O , CH), 3.64 (t, 1H, CH, $J = 6.95$ Hz), 3.85 (s, 2H, CH_2), 5.23 (t, 1H, CH, $J = 5.05$ Hz), 7.15 (m, 5H, CH), 7.69 (d, 4H, CH, $J = 7.53$ Hz), 8.24 (s, 1H, CH), 8.31 (s, 2H, CH), 10.30 (s, 1H, NH), 10.42 (s, 1H, NH) ppm, elemental analysis calculated for $\text{C}_{38}\text{H}_{24}\text{Br}_4\text{N}_4\text{O}_5$ (936.24 g/mol): C, 48.75%; H, 2.58%; N, 5.98%. Found: C, 48.53%; H, 2.77%; N, 6.04%.

RESULTS AND DISCUSSIONS

Monomer Synthesis

The synthetic route for the preparation of the diacid with a [3-phenyl-2-(tetrabromophthalimidy)propanoylamine] pendant group is depicted in Scheme 1. In the first step the reaction of L-phenylalanine with tetrabromophthalic anhydride in acetic acid afforded the imide acid 4. Compound 4 was reacted with thionyl chloride and the acid chloride 5 was obtained in high yield, which was subsequently reacted with 5-aminoisophthalic (6) acid in the presence of TEA in a typical low-temperature. The chemical structure and purity of compounds 4, 5 and diacid 7 were proven with FT/IR, ^1H NMR and ^{13}C NMR spectroscopic techniques and the spectra showed all the peaks which were in good agreement with the proposed structure and the results are shown in Table II. The ^1H NMR spectrum (500 MHz) of compound 7 is shown in Figure 1. The ^1H NMR spectrum of this diacid shows the characteristic absorption of C-H chiral center (dd), N-H amide groups and acidic O-H at 10.26, and 13.10 ppm, respectively. The purity of compounds 4 and 7 was checked by thin-layer chromatography, which showed one spot in ethylacetate/cyclohexane mixture (50:50). The structure of monomer 7 was also proven by elemental analysis.

Polymer Synthesis

Direct polycondensation of chiral dicarboxylic acid monomer 7 with aromatic diamines 8-15 using TPP and Py as

Figure 1. ^1H NMR (500 MHz) spectrum of monomer 7 in $\text{DMSO}-d_6$ at R.T.

condensing agent to form amide bonds was used as an efficient way to obtain PAs (1-16) of moderate to high degree of polymerization on a laboratory scale (Scheme 2). The polymerization reaction has been carried out both by thermal heating (method I) as well as microwave irradiation (method II) and the results are shown in Table III. The optimization of the reaction conditions by varying microwave power level, period of heating and amount of solvent were examined to provide polymers in high yield and molecular weight. The yields and

inherent viscosities of the polymers obtained by microwave irradiation verses thermal heating are comparable with remarkable reduction in reaction time due to homogeneous heating throughout the reaction media by microwave irradiation as compared to convection currents in thermal heating. A possible mechanism for the formation of these PAs is shown in Scheme 2.²⁶ All of the resulting PAs remained soluble in the reaction medium, thus permitting an increase their molecular weight and giving viscous solutions. Extended reaction time or higher power levels resulted in decreased yields and inherent viscosities for all PAs. This was due to decomposition of the reaction mixture. To avoid this trouble, the reactions were conducted with intermittent heating at a moderate power level with mixing. After the initial exposure for 90 s at power level 70% (630 W) the reaction mixture was taken out, mixed for 1 min and then heated at the same power level for an additional 30 s. This sequence was repeated until the formation of highly viscous solution. When the same experimental was conducted by microwave irradiation, it took 120 s for completion of polymerization reaction. When the same experiment was conducted by conventional heating, it took 5 h for completion of polymerization reaction. On the other hand, a more homogeneous heating and outstanding rate quickening were observed under microwave irradiation.

Polymer Characterization

The structure of the PAs was confirmed by FT/IR and ^1H NMR spectroscopy analysis. All these PAs exhibited absorption around $1660\text{--}1776\text{ cm}^{-1}$ are commonly attributed to the asymmetric and symmetric stretches of carbonyl groups. The presence of the imide heterocycle in these polymers was

Scheme 2. Polycondensation reactions of monomer 7 with different diamines.

Table III. Synthesis and some physical properties of PA1-PA16 prepared by method I^a and II^b

Method I ^a					Method II ^b				
Polymer ^c	Diamine	Yield (%)	η_{inh}^d (dL/g)	$[\alpha]_D^{25,d}$	Polymer ^c	Diamine	Yield (%)	η_{inh}^d (dL/g)	$[\alpha]_D^{25,d}$
PA1	8	87	0.58	-56.4	PA9	8	79	0.53	-40.1
PA2	9	80	0.44	-63.1	PA10	9	88	0.49	-31.4
PA3	10	76	0.45	-24.9	PA11	10	83	0.47	-51.4
PA4	11	83	0.31	-66.5	PA12	11	76	0.32	-49.5
PA5	12	64	0.48	-44.9	PA13	12	72	0.45	-49.7
PA6	13	82	0.63	-20.2	PA14	13	72	0.56	-21.0
PA7	14	81	0.39	-32.2	PA15	14	87	0.42	-31.0
PA8	15	89	0.50	-64.7	PA16	15	76	0.50	-84.3

^aMethod I: The reaction mixture was refluxed for 5 h under nitrogen atmosphere. ^bMethod II: The reaction mixture was irradiated in the microwave oven for 90 s then cooled and irradiated for 30 s again at 70% of its power level. ^cAll of these polymers were precipitated in methanol. ^dMeasured at a concentration of 0.5 g/dL in DMF at 25 °C.

Figure 2. ¹H-NMR (500 MHz) spectrum of PA8 in DMSO-*d*₆ at R.T.

revealed by absorption of 1375–1385 and 715–725 cm⁻¹ that belong to carbonyl's bending of imide. Bands of amide N-H groups appeared around 3300–3400 cm⁻¹. PA8 showed characteristic absorptions at 1156, 1338 cm⁻¹ due to sulfone group of diamine 15. Figure 2 show the ¹H NMR (500 MHz) spectrum of PA8. In the ¹H NMR spectrum of PA8, appearances of the N-H protons of amides groups at 10.34 and 10.88 ppm as two singlet peaks, respectively, indicate amide group in the polymer's side chain and main chain. The resonance of aromatic protons appeared in the range of 7.22–8.35 ppm. The proton of the chiral center appeared as doublet of doublet at 5.24 ppm. The results of elemental analysis were in good agreement with the calculated values. It is interesting to mention that polymer made by different methods (Table III) shows different optical rotation and this is consistent for the all types of diamines. These could be explained in terms of that optical rotation is highly dependent to the overall structure and regularity of the resulting polymer chains.

Figure 3. TGA thermograms of PA1, PA6, PA10 and PA11 under a nitrogen atmosphere at a heating rate of 10 °C/min.

Solubility Behavior of PAs

One of the main objectives of this study was producing modified PAs with improved solubility. The excellent solubility of these PAs compared with that of related aromatic PAs, which do not contain any pendent groups, is due to the presence of bulky side, containing Br group which prevents the packing of the macromolecules through hydrogen bonds between amides groups in the chain and thus facilitate the diffusion of solvent molecules among the polymer chains. The solubility of PAs was tested quantitatively in various solvents. All the PAs, were most readily soluble in organic solvents such as DMF, DMAc, dimethyl sulfoxide, NMP, Py and in H₂SO₄ at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol and water.

Thermal Properties

The thermal properties of PA1, PA6, PA10 and PA11 were evaluated by TGA/DTG and DSC at a heating rate of 10 and 20 °C/min, respectively, under a nitrogen atmosphere. All polymers showed almost similar decomposition behavior. Initial decomposition temperature, 5 and 10% weight loss temperatures (*T*₅, *T*₁₀), and char yields at 800 °C are summarized in (Figure 3 and Table IV). The DSC analyses for PAs showed *T*_g around 197–236 °C (Table IV). The temperatures of 5% weight loss for all the polymers ranged from 378 to 436 °C

Table IV. Thermal Properties of PA1, PA6, PA10 and PA11

Polymer	T_5 (°C) ^a	T_{10} (°C) ^b	Char Yield ^c	T_g (°C) ^d	LOI (%) ^e
PA1	385	453	48	197	68
PA6	422	449	52	225	70
PA10	378	409	48	212	65
PA11	436	495	58	236	67

^aTemperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min. in a nitrogen atmosphere. ^bTemperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min. in a nitrogen atmosphere. ^cPercentage weight of material left undecomposed after TGA analysis at a temperature of 800 °C in a nitrogen atmosphere. ^dGlass transition temperature was recorded at a heating rate of 20 °C/min in a nitrogen atmosphere. ^eLimiting oxygen index percent evaluating at char yield 800 °C.

and the residual weight at 800 °C ranged from 48 to 58% under nitrogen atmosphere. The high char yields of these PAs at high temperature region are important. It shows that these polymers have good thermal stability. The efficacy of brominated polymers as flame retardants is strongly dependent on their bromine content. It is notable that the major goal in this work is to improve flame resistancy of polymer. Structural modification of the polymer chains is an effective technique for improving flammability resistance. The thermal stability of a polymer is determined by the bond energy (resonance stability) between atoms on the main chain. Polymers containing large amounts of hydrogen, nitrogen or oxygen display high flammability because of their low bond enthalpy with carbon. The thermal stability of a polymer can be improved by increasing the strength of the chain bonds. Thermal stability is increased by incorporating aromatic and hetrocyclic ring structures with high resonance stabilization energies into the main chain, and minimizing the presence of H, N and O. Not only is the decomposition temperature of a polymer increased by this modification, but the mass fraction of flammable volatiles is reduced which lowers the heat release rate. BFRs work by releasing bromine free radicals when they are heated. Under thermal stress, BFRs release HBr, which it will inhibit the spreading of fire by substituting the reactive $H^\bullet$ and $HO^\bullet$ radicals in the radical-chain reaction for less reactive $Br^\bullet$ radicals. These free radicals scavenge other free radicals that are part of the flame propagation process and thus reduce the rate of flame expansion and the extent of fire damage (Scheme 3). Organobromine compounds are particularly well suited for this function because of the relatively low energy of the C-Br bond. When heated, these bonds break, and the relatively stable bromine free-radical is generated. Furthermore, the flame retardant property of these polymers was evaluated by measuring their LOI values. Van-Krevelen noted that the flammability of polymers containing C, H, N, O, and halogens, depends on a composition parameter (CP):

$$CP = (H/C) - 0.65 (F/C)^{1/3} - 1.1 (Cl/C)^{1/3} - 1.6 (Br/C)^{1/3}$$

where H/C, F/C, Cl/C and Br/C are element/carbon atomic ratios. The smaller the H/C ratio, the more aromatic is the polymer and the higher the LOI it exhibits. At $CP \geq 1$, polymers have $LOI = 0.175$; at $CP < 1$, $LOI = 0.60 - 0.425 CP$. Resulting data showed LOI percent data between 65 and

Scheme 3. Mechanism of action of brominated flame retardants. **Figure 4.** Determination of kinetic parameters of PA1 by plots of the left part in eq (16) against $-1/T$ using differential method.

70. Generally, materials exhibiting LOI percent values greater than 28 would show self-extinguishing behavior and were considered to be flame retardant.^{20–27} Therefore high char yields data, along with good LOI percent values between 48 and 58, indicated that these polymers have good flame retardant properties (Table IV).

Kinetic Study of Thermal Decomposition of Synthesized PAs

The objective of this analysis is to compare the kinetic parameters were calculated by the classic integral and differential methods. In order to determine which degradation mechanism of synthesized PAs are in the best agreement with the data, the obtained activation energies were compared. The calculated reaction order at the best correlation coefficients values are just our required one. The best overall fit values were obtained by using $n = 1.0$ for differential method (Figure 4). As the values of the correlation coefficients of the aforementioned mechanisms presented approximate values, the identification of the mechanism of thermal decomposition reaction in the solid state was carried out by the comparison of the fits between the theoretical and experimental data. By comparison of the results with the values obtained by Criado method we found the mechanism which best describes the thermal decomposition of PAs corresponding to the mechanism F1 (Random nucleation with one nucleus on the individual particle). The $Z(\alpha)$ master curves can be plotted using eq (17)

Figure 5. Determination of thermo-oxidative degradation reaction mechanism by plots of $Z(\alpha)$ versus α using Criado methods for PA1.

Table V. Results of the kinetic analysis of the thermal decomposition curve for the PA1, PA6, PA10 and PA11 by different methods

Polymer	Differential		Coats-Redfern		Van-Krevelen	
	E (kcal mol ⁻¹)	r	E (kcal mol ⁻¹)	r	E (kcal mol ⁻¹)	r
PA1 (353-487)	11.62	0.997	10.95	0.997	10.77	0.995
PA6 (387-534)	22.46	0.999	22.29	0.995	24.27	0.997
PA10 (366-500)	12.80	0.998	12.23	0.997	12.05	0.997
PA11 (370-520)	18.36	0.998	18.05	0.999	17.26	0.997

according to different reaction mechanisms $g(\alpha)$ shown in Table I. Here, the used experimental TG data are still from TG curve at 10°C/min heating rate. Accordingly, the $Z(\alpha)$ experimental curves can be plotted using eq (18). Figure 5 shows the $Z(\alpha)$ master and experimental curves of PA1, PA6, PA10 and PA11. As can be seen, the experimental curve of aforementioned PAs (Figure 5) nearly overlaps the master curve $Z(F1)$, indicating that the thermal oxidative degradation of four PAs belongs to F1 reaction mechanism. Because the solid-phase reaction obeying F1 mechanism often has the feature of 1-order kinetics, the thermal oxidative degradation of resulting polymers is a 1-order kinetic reaction, which is in accordance with the result obtained by classic integral and differential method. This curve has been analyzed by means of the differential and integral methods by assuming an F1 kinetic model. For the integral analysis, the two different approaches analyzed here have been used. Table V includes the resulting values of the activation energy and correlation coefficient, as calculated by assuming the value of E obtained from differential method as the correct one because no approximation is used for deriving eqs (1) and (2) as well as the integral method. The r was computed using the least squares method, by plotting the left-hand side of the eqs (16) and (8) versus $-1/T$ (Figure 4 and Figure 6) and eq (13) versus $\ln T$ (Figure 7), respectively.¹⁻⁸ The n value which gave the best fit ($r = 1$) was chosen as the order parameter for the decomposition stage of interest. From the intercept and linear slope of such stage, the A and E values were determined, the other kinetic parameters, ΔS (entropy of activation), ΔG (Gibbs free energy) and ΔH (enthalpy of activation) were computed using the relationships:

Figure 6. A typical plots of $\ln[-\ln(1-\alpha)/T^2]$ against $-1/T$ for PA1, PA6, PA10 and PA11.

Figure 7. A typical plots of $\ln[-\ln(1-\alpha)]$ against $\ln T$ for PA1, PA6, PA10 and PA11.

Table VI. Kinetic parameters for the degradation of PAs determined using the differential method

Polymer	Parameter			
	A (s ⁻¹)	ΔS (kcal mol ⁻¹ K ⁻¹)	ΔH (kcal mol ⁻¹)	ΔG (kcal mol ⁻¹)
PA1 (353-487)	0.36	-0.06	10.38	49.16
PA6 (387-534)	315.47	-0.05	21.09	50.55
PA10 (366-500)	1.53	-0.06	11.53	49.36
PA11 (370-520)	257.89	-0.05	17.06	49.15

$\Delta S = R[\ln(Ah/kT)]$, $\Delta H = E - RT$ and $\Delta G = \Delta H - T\Delta S$, where A is the Arrhenius parameter, k is the Boltzmann's constant and h is the Planck's constant. The values of the thermodynamic parameters of activation are given in Table VI. The negative values suggest that the segment undergoes some chain alignment at elevated temperatures forming the activated complex. The positive values of ΔH indicate that the dissociation processes are endothermic in nature and enhanced with the rise of temperature. ΔG values for the dissociation constants are positive, thus dissociation processes are non-spontaneous.²⁸⁻³⁰

Estimation of Half-Life Time, $t_{1/2}$ and Lifetime, t_f

A major application of TG and DTG kinetic parameters is

Table VII. Rate constant k of thermal degradation, half-life time and estimated lifetime for synthesized PAs at different temperatures in nitrogen atmosphere

T (°C)	PA1		PA6		PA10		PA11	
	Lifetime ^a	Half-life time ^a	Lifetime ^a	Half-life time ^a	Lifetime ^a	Half-life time ^a	Lifetime ^a	Half-life time ^a
300	63.1	852.8	966.3	13053.4	41.8	564.6	32.5	438.6
400	14.0	187.7	51.8	700.3	7.9	106.6	3.0	40.1
500	4.5	61.1	5.9	80.1	2.3	31.0	0.5	6.8
600	1.9	25.7	1.1	15.0	0.9	12.0	0.1	1.7
700	0.9	12.9	0.3	4.0	0.4	5.6	0.04	0.6
800	0.6	7.4	0.1	1.3	0.2	3.0	0.02	0.2

^aLifetime and Half-life time in (min⁻¹).

to predict the maximum usable temperature, the optimum processing temperature regions, and the estimated lifetime of the polymers. It offers a simple and convenient approach to use as an accelerated ageing process for quality control experiments. Resulting polymers obeys a degradation mechanism, F1, where $f(\alpha) = (1 - \alpha)^n$, and taking into account the activation energy and pre-exponential value obtained by differential method. The decomposition kinetics at elevated temperature could be extrapolated back to the service conditions for which the lifetime prediction is required. After a specific period of time, the half-life time, $t_{1/2}$, is defined as the value of α becomes 0.50 and the lifetime, t_f , of polymer to failure is generally defined to be when the degree of decomposition reaches 0.05. This equation allows the calculation of the lifetime and half-life time as a function of temperature through the constant rate k , and results are shown in Table VII. Synthesized flame-retardant PAs, as the most of the polymers, obeys at a mechanism of decomposition type F1, and in this case, the half-life time and the lifetime are calculated^{6,7} by eq (23).

$$t_{1/2} = \frac{0.693}{k} \quad \text{and} \quad t_f = \frac{0.0513}{k} \quad (23)$$

CONCLUSIONS

In summary, we have developed an efficient, convenient and practical approach for the synthesis of thermally stable aromatic optically active PAs using microwave irradiation as well as conventional heating. A comparable result on the isolated yields and inherent viscosities was obtained by microwave irradiation versus thermal heating with substantial reduction in reaction time. In this work by use of chiral aromatic dicarboxylic acid 7, containing a rigid tetrabromophthalimide and flexible L-phenylalanine group, a series of optically active aromatic PAs with flame retardancy properties was prepared. TPP and Py in NMP system was effectively applied for direct polycondensation of diacid 7 with various aromatic diamines. The main advantage of this polycondensation reaction is that this procedure is a one-pot reaction and we do not need to prepare diacid chloride. The resulting PAs have L-phenylalanine in polymer chain and are optically active. The introduction of pendent bulky chiral groups along the polymer backbone results in a less ordered polymer matrix, therefore

disturbed the strong interchain forces and inherent macromolecular rigidity and consequently increasing the solubility characteristics without affecting thermal properties to any great extent. These PAs could be considered as new processable high-performance polymeric materials. In addition, because of the presence of amino acids as pendent groups, these polymers are expected to be bio-reactive and therefore are classified under environmentally friendly polymers. Since the resulting polymers are optically active and have good thermal stability they have potential to be used as a chiral stationary phase in chromatography technique for the separation of racemic mixtures. On the basis of TG/DTG results obtained at a single heating rate, some important kinetic parameters of thermal degradation for the resulting PAs, such as activation energy, degradation order, and frequency factor, have been easily calculated by the integral methods as well as differential method. The kinetic data in nitrogen suggest that synthesized PAs exhibits good thermostability. The differential method provides the activation energies without any assumption about the reaction order whereas the two other methods used (Coats-Redfern and Van-Krevelen) require a prior knowledge of the reaction mechanism of the decomposition. The reaction mechanisms were determined by Criado method. The kinetic parameters were used to predict the half-life time and the lifetime at different temperatures, based upon thermal degradation. The calculations show that the PAs can be used at room temperature for a very long time without failure. It must be stressed that these calculations predict the expected lifetime on the PAs systems based only on thermal degradation data.

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REFERENCES

1. S. Francis, L. Varshney, and S. Sabharwal, *Eur. Polym. J.*, **43**, 2525 (2007).

2. L. A. Pérez-Maqueda, P. E. Sánchez-Jiménez, and J. M. Criado, *Polymer*, **46**, 2950 (2005).
3. K. K. Yang, X. L. Wang, Y. Z. Wang, B. Wu, Y. D. Jin, and B. Yang, *Eur. Polym. J.*, **39**, 1567 (2003).
4. G. R. Heal, *Thermochim. Acta*, **340–341**, 69 (1999).
5. L. Núñez, F. Fraga, M. R. Núñez, and M. Villanueva, *Polymer*, **41**, 4635 (2000).
6. L. Barral, J. Cano, J. López, I. López-Bueno, P. Nogueira, M. J. Abad, and C. Ramírez, *Eur. Polym. J.*, **36**, 1231 (2000).
7. L. Barral, F. J. Díez, S. García-Garabal, J. López, B. Montero, R. Montes, C. Ramírez, and M. Rico, *Eur. Polym. J.*, **41**, 1662 (2005).
8. T. Wanjun, L. Yuwen, Z. Hen, W. Zhiyong, and W. Cunxin, *J. Therm. Anal. Calorim.*, **74**, 309 (2003).
9. S. Mallakpour and M. Taghavi, *Eur. Polym. J.*, **44**, 87 (2008).
10. S. Mallakpour and H. Seyedjamali, *Amino Acids*, **34**, 531 (2008).
11. S. Mallakpour and F. Rafiemanzelat, *Eur. Polym. J.*, **41**, 2945 (2005).
12. S. Mallakpour and M. Kolahdoozan, *React. Funct. Polym.*, **68**, 91 (2008).
13. S. H. Hsiao and Y. H. Chang, *Eur. Polym. J.*, **40**, 1749 (2004).
14. G. S. Liou, H. J. Yen, Y. T. Su, and H. Y. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 4352 (2007).
15. T. Temma, M. Kobayashi, Y. Agata, T. Yamane, J. Miura, and M. Takeishi, *J. Polym. Sci., Part A: Polym. Chem.*, **42**, 4607 (2004).
16. S. Mallakpour and Z. Rafiee, *Polymer*, **48**, 5530 (2007).
17. S. Mallakpour and Z. Rafiee, *Polym. J.*, **39**, 1185 (2007).
18. S. Mallakpour and M. Taghavi, *Polymer*, **49**, 3239 (2008).
19. S. Mallakpour and E. Kowsari, *J. Polym. Sci., Part A: Polym. Chem.*, **41**, 3974 (2003).
20. "Fire retardant materials," A. R. Horrocks and D. Price, Ed., England, Woodhead Publishing Ltd, 2001.
21. R. M. Aseeva and G. E. Zaikov, *Adv. Polym. Sci.*, **70**, 171 (1985).
22. S. Huber and K. Ballschmiter, *Fresenius' J. Anal. Chem.*, **371**, 882 (2001).
23. L. Li, C. Guan, A. Zhang, D. Chen, and Z. Qing, *Polym. Degrad. Stab.*, **84**, 369 (2004).
24. E. Botines, L. Franco, and J. Puiggali, *J. Appl. Polym. Sci.*, **102**, 5545 (2006).
25. S. Vyazovkin, *J. Therm. Anal. Calorim.*, **83**, 45 (2006).
26. N. Yamazaki, F. Higashi, and J. Kawabata, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2149 (1974).
27. D. W. Van Krevelen and P. J. Hoftyzer, "Properties of polymers," 3rd ed., Elsevier Scientific Publishing, 1997.
28. M. N. Radhakrishnan Nair, G. V. Thomas, and M. R. Gopinathan Nair, *Polym. Degrad. Stab.*, **92**, 189 (2007).
29. M. S. Refat and A. A. Ibrahim, *Spectrochim. Acta, Part A*, **70**, 234 (2008).
30. M. S. Refat, A. M. El-Didamony, and I. Grabchev, *Spectrochim. Acta, Part A*, **67**, 58 (2007).
31. S. Mallakpour and M. Taghavi, *React. Funct. Polym.*, in press.