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Obtaining kinetic parameters of polyamide imide reaction

Obtención de parámetros cinéticos de la reacción de poliamida imida

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Abstract

A kinetic study for the synthesis of polyamide-imide (PAI) is presented, determining the instantaneous intrinsic viscosity [η] at different reaction times, in order to assess the influence of the order of addition in the reactants 1,2,4-benzenetricarboxylic anhydride (TMA) and diphenylmethylene diisocyanate (MDI) on the chemical structure and on the thermal properties of PAI. The kinetic parameters determined were the reaction order, n, the constant rate, k, and the activation energy, E_a. The reaction was carried out at different temperatures from 110 to 150 °C at 30 % solids in N-methyl-2-pyrrolidone (NMP) as solvent. The chemical structure of the polymer was determined by ^{1}H-NMR, FTIR and elemental analysis; other properties such as the glass transition temperature (T_g), onset temperature of weight loss rate (T_0) and temperature of maximum weight loss rate (T_{max}) obtained by DSC and TGA/DSC were used to explain the most likely distribution of arrangements II, AA and AI along the chain of PAI based on thermal stability.

Keywords: Order of addition, polyamide imide, instantaneous intrinsic viscosities, reaction kinetics, kinetic data analysis methods, diisocyanate.

Resumen

Se presenta un estudio cinético para la síntesis de poliamida-imida (PAI), determinando la viscosidad intrínseca instantánea [η] a diferentes tiempos de reacción, con el fin de evaluar la influencia que presenta el orden de adición de los reactivos anhídrido 1,2,4-bencenotricarboxílico (TMA) y difenilmetilen diisocyanate (MDI) sobre la estructura química y sobre las propiedades térmicas de la PAI. Los parámetros cinéticos determinados fueron el orden de reacción, n, la constante de velocidad, k, y la energía de activación, E_a. La reacción se llevó a cabo a distintas temperaturas desde 110 hasta 150 °C al 30% de sólidos. La estructura química del polímero se determinó a partir de RMN[1]H, FTIR y análisis elemental; otras propiedades como la temperatura de transición vítrea (T_g), la temperatura inicial de la velocidad de pérdida de peso (T_0) y la temperatura de la velocidad máxima de pérdida de peso (T_{max}) obtenidas por DSC y TGA/DSC fueron utilizadas para explicar la probable distribución de arreglos II, AA and AI a lo largo de la cadena de PAI con base en la estabilidad térmica.

Palabras clave: Orden de adición, poliamida imida, viscosidades intrínsecas intantáneas, cinética de reacción, métodos de análisis de datos cinéticos, diisocianatos..

1 Introduction

Although polyamide-imide (PAI) is a widely studied polymer, it still belongs to the type of high-performance thermoplastic resins used as wire enamels and composites, due to its excellent thermal and chemical properties (Atanu *et al*., 1983; Shen Chou *et al*., 2002; Murray 2008; Kikuchi *et al*., 2011; Haiyang Shi *et al*., 2013; Biaobing *et al*., 2016). The improvement of thermal properties with respect to polyamide (PA), by the incorporation of

an imide group in the structure, prevents degradation in high temperatures making it more resistant. On the other hand, the incorporation of the amide group improves the processability of the material allowing its thermoforming (Chen *et al*., 1996). Currently, there are several synthesis routes proposed by various research groups to obtain PAI, some of them used as precursors to the diamines (Holub *et al*., 1969 and 1975; Incremona *et al*., 1974; Flowers *et al*., 1975; Imai *et al*., 1985; Takuya *et al*., 2010; Shunchang *et al*., 2018) whose main intermediary is the polyamic acid, when is dehydrated, produces the cyclization for the formation of the imide group.

Others use diisocyanates; which generate carbon dioxide as a by-product of the reaction when PAI is formed (Zecher *et al.*, 1969; Izumi *et al.*1974; Sintes-Zydowicz *et al.*, 1993; Kikuchi *et al.*, 2011; Saotome *et al.*, 2012). It is important to have concrete knowledge about experimental conditions when it is working with polycondensation reactions, in order to promote the formation of a particular chemical structure and to visualize its potential applications (López-Badillo *et al.*, 2018). Yuhong-Qi and coworkers studied in detail the synthesis of PAI (ratio of reactants, synthesis time, heating rate and reaction temperature) based on 4,4'-diphenylmethane diisocyanate (MDI) as well as the mechanical properties of PAI films (Yuhong-Qi *et al.*, 2017).

However, despite the extensive study in the synthesis of this polymer, only one kinetic study reported by Ho and collaborators has been found, they proposed the use of MDI derivatives in excess with anhydride phthalic and benzoic acid (Ho *et al.*, 1997).

There are several publications addressing kinetic studies applied to different areas of knowledge, for example for food area in imbibition kinetics and moisture sorption isotherms (Domínguez *et al.*, 2007), growth and fatty acid profile (Navarro *et al.*, 2017), production of mezcal, enzymatic esterification and stability of antioxidants (Luna *et al.*, 2007; Correa *et al.*, 2017; Solís *et al.*, 2017), thermoxidation of milk fat and chlorogenic acid degradation (Martinez *et al.*, 2018; Ruiz *et al.*, 2019;); or for materials in steel corrosion, degradation of ethers and dyes (Cuevas *et al.*, 2006; Ayala *et al.*, 2017; Félix *et al.*, 2017), modeling isothermal cure, swelling of hydrogels, pyrotechnic compositions and chemical polymerization (Martínez *et al.*, 2007; Aguilar *et al.*, 2013; Yang Tan *et al.*, 2013; Chatterjee *et al.*, 2017; Ambekar *et al.*, 2018; Fang *et al.*, 2018).

Three synthesis routes based on the order of addition of reactants were studied in this research, as well as the observed effect of imide (I) and amide (A) groups distribution along the chains. In addition, the description of the kinetic parameters of each synthesis route is presented, these were related to chemical structure and to the thermal properties obtained by DSC and TGA/DSC.

2 Materials and methods

2.1 Materials

For the polymerization synthesis, commercial reactants provided by Sigma-Aldrich Chemical were used; diphenylmethylene diisocyanate [MDI, CAS 101-68-8], 1,2,4-benzenetricarboxylic anhydride [TMA, CAS 552-30-7] and N-methyl-2-pyrrolidone [NMP, CAS 872-50-4]. The MDI and the TMA were recrystallized twice, using chloroform and toluene respectively. Subsequently this, they were dried under vacuum for two hours. The NMP solvent used for the synthesis and the dimethylformamide [DMF, CAS 68-12-2] occupied for the viscosimetric characterization were dried by vacuum distillation for a period of two hours to eliminate any traces of moisture. The water content of 269 and 326 ppm respectively, was determined by Karl Fischer analysis.

2.2 Instruments

For the synthesis of PAI resin, a system equipped with a 150 mL round bottom five-necked flask was assembled inside a heating blanket, it was connected to a Digi-Sense of Cole Palmer Instrument Company temperature controller with J-type thermocouple (whose sensitivity was $\pm 1 \,°$ C), it also consisted of a nitrogen gas inlet tube, an arrow mechanical stirrer model 850 with 1/8" glass arrow and 2 cm long plastic propellers. Infrared spectroscopy characterization was carried out in a Nicolet 510P FT-IR device with a spectral resolution of 4 cm^{-1}. The nuclear magnetic resonance was carried out on a Varian-Unity nuclear magnetic resonance 300 MHz spectrometer in DMSO-d_6. The elemental analysis of the compounds was performed in an elemental analyzer 2499 C, H, N series II by Perkin Elmer. The instantaneous intrinsic viscosities of all polymers were carried out using an Ubbelohe No. 1C capillary viscometer and a Cannon Instruments 5010 thermostating system to maintain the temperature at 25 °C. Thermal analyses were performed on two devices, a DSC2010 and a TGA/DSC SDT Q600, both TA Instruments.

2.3 Synthesis of poly(amide-imide)

The synthesis was carried out according to several patents (Zecher *et al.*, 1969; Izumi *et al.*, 1974; Sintes-Zydowicz *et al.*, 1993; Barikani *et al.*, 1999; Kikuchi *et al.*, 2011; Yuhong-Qi *et al.*, 2017). The reaction

consists of a mixture of TMA (19.76 g, 0.103 mol), MDI (25.74 g, 0.103 mol) and dry NMP (84.50 g, 0.852 mol). The compounds were mixed following three proposed synthesis routes at 110, 127, 140 and 150 °C based on the addition order of monomers:

a) *PAI*-1: MDI/NMP solution, to later add TMA. TMA was added into the MDI/NMP solution in small portions over a period of 5 min at 140 °C (carbon dioxide gas was observed at this temperature).

b) *PAI*-2: TMA/NMP solution, to later add MDI. MDI was added into the TMA/NMP solution in small portions over a period of 5 min at 140 °C (carbon dioxide gas was observed at this temperature).

c) *PAI*-3: MDI/TMA solution in NMP. MDI and TMA were added into the reaction flask with NMP since the beginning of the synthesis.

Each synthesis route was prepared at constant temperature undergoing 24 hours of vigorous stirring, nitrogen atmosphere was maintained in the reaction flask throughout the course of the reaction. The PAI product was precipitated by adding ethanol, then it was filtered and purified in a Soxhlet apparatus, the purification takes place for a period of 8 hours with the same solvent, to be dried later under vacuum at 190 °C for 12 hours. Obtaining a percentage of yield of 87, 90 and 88%, respectively.

2.4 Kinetic analysis

The polymerization kinetic was followed determining the instantaneous intrinsic viscosity $[\eta]$ at different reaction times, t_1. Sampling was done by taking aliquots from 20 minutes to 24 hours. With each sample of precipitated PAI previously purified in a Soxhlet apparatus and dried under reduced pressure (procedure outlined in section 2.3), solutions were prepared in DMF at a concentration, C, of 0.5 g/dL. The time of pouring the solvent and each solution was obtained by maintaining the temperature at (25.0 ± 0.1) °C using a thermostated water bathing. The relative viscosity (η_{rel}) and specific viscosity (η_{sp}) allowed to calculate $[\eta]$ applying the equation of Solomon-Ciuta. It was formulated with the expressions of Huggins and Kramer (Solomon *et al.*, 1962; Douglas *et al.*, 2007), Eq (1).

$$[\eta] = \frac{[2(\eta_{sp} - \ln \eta_{rel})]^{1/2}}{C} \tag{1}$$

The conversion (X) was calculated by relating each $[\eta]$ at different reaction times with $[\eta]_f$, value obtained at 24 hours. With the same equation was calculated the concentration of [PAI] produced for each time, where $[MDI]o$ is the initial concentration of MDI

$$X = \frac{[\eta]}{[\eta]_f} = \frac{[PAI]}{[MDI]_o} \tag{2}$$

[PAI] plotted against t_1 was used to determine the reaction orders n, and the rate constants k (M^{-1} s^{-1}), for which the integral, differential and Powell methods were applied; Eqs (3)-(5) respectively (Levine *et al.*, 2004).

$$\frac{1}{[MDI]} = kt_1 + \frac{1}{[MDI]_o} \tag{3}$$

$$\ln\left(-\frac{d[MDI]}{dt}\right) = \ln k + n\ln[MDI] \tag{4}$$

$$\alpha^{1-n} - 1 = \phi(n-1) \ to \neq 1 \tag{5}$$

where $\alpha = [MDI]/[MDI]_o = (1-X)$; $\phi = kt_1[MDI]_o^{n-1}$ and $[MDI]$ is the concentration of MDI at t_1.

The activation energy E_a (kJ mol^{-1}) can be calculated from Arrhenius equation, a plot of $\ln k$ versus $1/T$.

2.5 Thermal analysis

A DSC2010 device (previously calibrated for energy and temperature with high purity indium under a dry constant-flow nitrogen atmosphere) was used to determine the vitreous transition temperature (T_g). Three scans were carried out of each PAI with approximately 2 mg, the method log was: ramp 15 °C/min to 380 °C.

A TGA/DSC SDT Q600 device (previously calibrated for mass, temperature and heat flow) was used to research the behavior of PAI samples under a dry constant-flow nitrogen atmosphere. Approximately 10 mg of sample was occupied, the method log was: ramp 10 °C/min in the range temperature from 100 to 1100 °C.

3 Results and discussion

3.1 FTIR, ^{1}H-NMR and elemental analysis

Unlike Ho and colleagues (Ho *et al.*, 1997) whose reaction was followed at 2:1 molar ratio of TMA:MDI,

in the present work the conventional chemical reaction for the formation of polyamide-imide (PAI) was based on the interaction of TMA with MDI in NMP at a 1:1 molar ratio of TMA:MDI, the temperature remained constant in each synthesis routes at 110, 127, 140 and 150 °C in nitrogen atmosphere for a period of 24 hours. The appearance within the first 10 minutes of reaction was faint orange color, after this time it began to change to a dark brown color which remained until the reaction ended (unlike the polymer of Sintès (Sintès *et al.*, 1993) who added benzoic acid into the reaction, obtaining a yellow powder).

PAI-3 synthesis (in which the reactants were added at the beginning, MDI/TMA solution in NMP) was the most stable from beginning to end of the synthesis, in contrast to *PAI*-1 (MDI/NMP solution, adding subsequently TMA) and *PAI*-2 (TMA/NMP solution, adding afterwards MDI). The addition of the second reactant caused a spontaneous release of CO_2 and therefore a lack of control in the temperature, which was stabilized after 5 min. In the three synthesis routes the characteristic dark brown color was observed. The precipitate in the form of purified and dried PAIs' dust (PAIs to refer three synthesis route) was used both to determine the chemical structures by FTIR, ^{1}H-NMR and Elemental Analysis, and to quantify the instantaneous intrinsic viscosities at 25 °C in DMF obtaining values of 0.33 dL·g^{-1} for *PAI*-1 and *PAI*-2, and 0.35 dL·g^{-1} for *PAI*-3. Figs. 1 and 2 show the FTIR and ^{1}H-NMR spectra of PAIs. The infrared spectra of all the PAIs confirm the presence of I (imide) and A (amide) groups, FTIR (cm^{-1}): 3363 (*v*NH, amide), 3034 (*v*CN, amide), 1778 (*v*C=O, imide), 1660 (*v*C=O, amide I), 1599 (*v*C=C Ar), 1511 (*v*CN, amide II), 1374 (*v*CN, imide II), 1255 (*v*CNH, amide III), 1088 (*v*CNC, imide III), 723 (*v*CNC, imide IV).

Sintès and colleagues (Sintès *et al.*, 1993) have studied the microstructure of PAI by ^{1}H- and ^{13}C-NMR. They found that the repartition of I (imide) and A (amide) groups along the chains is random. Their formulation was 1.25 mol of MDI, 1 mol of TMA and 0.5 mol of benzoic acid in NMP at 180 °C. In our ^{1}H-NMR spectra for *PAI*-1, *PAI*-2 and *PAI*-3 at 140 °C, the recurrent unit contains nine signals (denoted with numbers from 1 to 9), Fig. 2. ^{1}H-NMR (300 MHz, DMSO-*d*$_6$) δ(ppm): 10.6 (m, 1H, -NHCO-); 7.1-8.9 (m, 11H, H-Ar); 4.0 (m, 2H, -CH$_2$-).

The integration of the seven signals observed between 7.1 and 8.9 ppm corresponds to the eleven types of heterotopic protons linked to the aryl functional groups. The signal that appears in 10.6 ppm

corresponds to the amide functional group which is integrated by one proton. In the case of the signal that appears in 4.0 ppm, it is integrated by two protons, the methylene proton resonances show the distribution of II (imide-imide) at 4.09 ppm, AI (amide-imide) at 4.00 ppm and AA (amide-amide) at 3.91 ppm, Fig 3. The characterization by elemental analysis was determined in two ways. In the first, the sample of each PAI ($C_{22}H_{14}N_2O_3$) synthesized at 140 °C, previously purified and dried at 190 °C for 12 hours and stored in argon atmosphere showed the following results: *PAI*-1 (calculated) found: %C (74.57) 74.22, %H (3.98) 4.10, %N (7.91) 7.68; *PAI*-2 (calculated) found: %C (74.57) 74.42, %H (3.98) 4.10,%N (7.91) 7.63; *PAI*-3 (calculated) found: %C (74.57) 74.81, %H (3.98) 3.91, %N (7.91) 7.71.
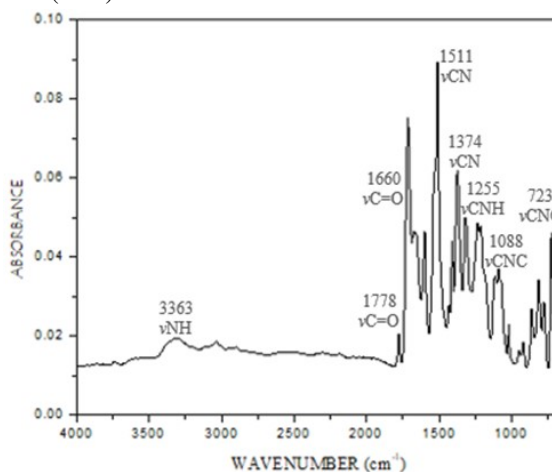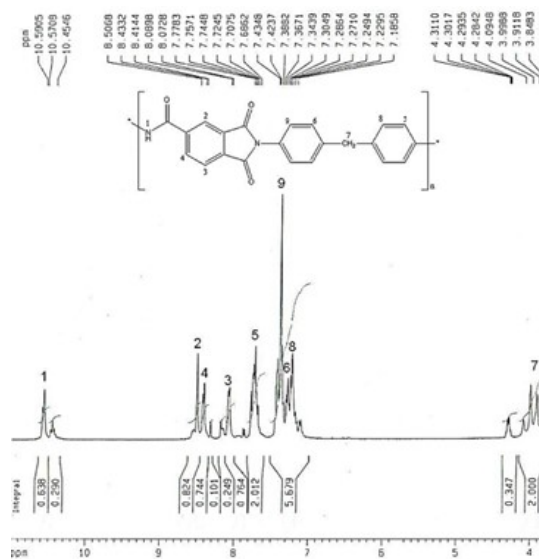

Fig. 1. 1 FTIR spectra of PAIs.

Fig. 2. ^{1}H-NMR spectra of PAIs.

Table 1. Elemental analysis of PAI.

Polymer	Formula (mol. weight)[b]	Elemental analysis[a]					
		%C (calcd)	found corrected	%H (calcd)	found corrected	%N (calcd)	found corrected
PAI-1			72.45		4.18		7.50
			74.54		4.06		7.72
PAI-2	$(C_{22}H_{14}N_2O_3)_n$ $(354.38)_n$	74.57	72.53	3.98	4.11	7.91	7.58
			74.55		4.00		7.79
PAI-3			72.46		4.15		7.60
			74.50		4.03		7.81

[a] Corrected values for C and N = found value x (100% + % moisture uptake). Corrected value for H = found value x (100% -% moisture uptake). %Moisture uptake = $\frac{W-W_o}{W_o}$ x 100%, where W is the weight of the PAI sample after being exposed to the environment for 10 min, and W_o is the weight of the PAI sample after being dried in vacuum at 140 °C for 12 hours. The values of % moisture uptake were: 2.88, 2.79 and 2.81for *PAI*-1, *PAI*-2 and *PAI*-3 respectively.

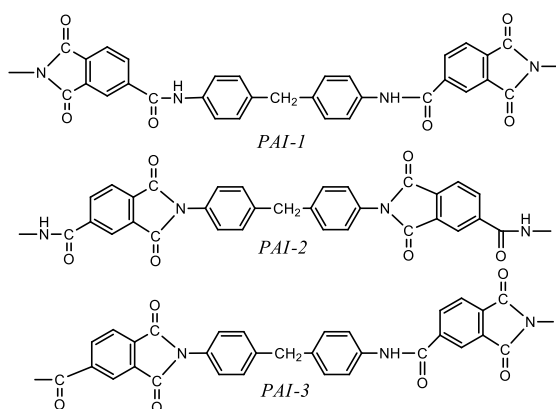[b] Molar masses are based on 2013 IUPAC recommendations (Meija *et al.*, 2016).

Fig. 3 Repartition of II, AA and AI units along the chains of PAI.

Table 2. Kinetic values for PAI-1 at 140 ℃.

t_1, s	t_2, s[a]	$[\eta]$[b], dL g^{-1}	X[c]	[PAI-1][d]
0	0	0.0000	0.0000	0.0000
1200	34.2	0.1409	0.4238	0.3759
1800	34.8	0.1766	0.5312	0.4712
3180	35.7	0.2294	0.6900	0.6121
4080	35.9	0.2410	0.7250	0.6431
5880	36.3	0.2641	0.7945	0.7048
9480	36.7	0.2870	0.8635	0.7660
13080	36.9	0.2985	0.8978	0.7964
43200	37.3	0.3211	0.9661	0.8570
86400	37.5	0.3324	1.0000	0.8871

[a] Pouring times using an Ubbelohe No. 1C capillary viscometer and a Cannon Instruments 5010 thermostating system to maintain the temperature at 25 ° C. The pour time of the DMF solvent was t_o=31.9 s.

[b] The instantaneous intrinsic viscosity was calculated according equation 1, where $\eta_{sp} = (t_2 - t_o)/t_o$ and $\eta_{rel} = t_2/t_o$

[c] Conversion was calculated by applying equation 2.

[d] [PAI-1] =X·[*MDI*]$_o$, where [*MDI*]$_o$= 0.8871M.

On the other hand, each polymer sample was exposed to the environment for a period of 10 minutes, the results of elemental analysis are listed in Table 1. The hygroscopic nature of each of the three samples was found within the range of 2.76 to 2.81%, which was obtained through comparing the mass difference between the PAI exposed to the media environment (for a period of 10 minutes) and the PAI dried under vacuum (at 190 °C for 12 hours). The corrected values were in accordance with the calculated values (Ching-Ping *et al.*, 1999).

3.2 Kinetic analysis

Once the PAIs were characterized to know the chemical structure, we proceeded to determine their kinetic studies in order to explain the most favorable chemical arrangement for each synthesis route. Table 2 shows a representative kinetic for *PAI*-1 at 140 °C where the maximum of $[\eta]$ reached at 24 hours was 0.3324 dL g^{-1}. Table 3 exhibits the kinetic parameters for PAIs at 140 °C by applying the integral, differential and Powell methods.

Ho and colleagues (Ho *et al.*, 1997) performed a PAI reaction kinetic via BMDI (*p*-chlorophenol blocked diphenylmethylene diisocyanate) with TMA at a 1:2 molar ratio.

They found out that the reaction order for the formation of the amide group had a value of 1 and for the formation of the imide group had a value of 2. According to this research, when the molar ratio of MDI with TMA is performed at a molar ratio 1:1, a reaction order of 1.920 is obtained for *PAI*-1, of 1.927 for *PAI*-2 and of 1.931 for *PAI*-3. That is, the reaction is approximately second order regardless of the order of addition in the reactants, Table 4.

Table 3. Values of *n* and *k* ($M^{-1} s^{-1}$) at 140 °C calculated by integral, differential and Powell method.

Route	Integral			Differential			Powell		Average	
	n	*k*	*r*	*n*	*k*	*r*	*n*	*k*	*n*	*k*
PAI-1	2	0.0007	0.9999	1.755	0.0006	0.9782	2	0.0007	1.918	0.0007
PAI-2	2	0.0007	0.9997	1.775	0.0006	0.9757	2	0.0007	1.925	0.0007
PAI-3	2	0.0008	0.998	1.717	0.0008	0.9687	2	0.0008	1.906	0.0008

Table 4. Kinetic parameters of PAIs at all temperatures.

	PAI-1		*PAI-2*		*PAI-3*	
T, K	k_1	n_1	k_2	n_2	k_3	n_3
382.15	0.0003	1.862	0.0003	1.862	0.0003	1.900
400.15	0.0004	1.946	0.0005	1.95	0.0005	1.953
413.15	0.0007	1.918	0.0007	1.925	0.0008	1.906
423.15	0.0011	1.953	0.0012	1.972	0.0012	1.963
n, average[a]:	1.920±0.041		1.927±0.048		1.931±0.032	
E_a, kJ mol^{-1}:	42.37		43.36		45.04	

[a] The uncertainties correspond twice the overall standard deviation of the mean.

For activation energy E_a, values of 42.37, 43.36 and 45.04 kJ mol^{-1} were obtained for *PAI*-1, *PAI*-2 and *PAI*-3 respectively, unlike Ho and co-workers who obtained a value of 91.21 kJ mol^{-1} from BMDI in excess PA (phthalic anhydride). As can be seen in Table 4, the three synthesis routes have an influence on E_a, not the other kinetic parameters (*n* and *k*). Experimentally the *PAI*-3 synthesis showed a controlled detachment of CO_2 from beginning to end of the reaction, this can be related to the higher value of E_a, allowing higher molecular weights ($[\eta] = 0.35$ dL g^{-1}) in comparison to the other two synthesis routes. On the other hand, gradually adding MDI in a saturated TMA solution will favor the arrangement II (imide-imide) similar to the molar ratio 2:1 of TMA: MDI proposed by Ho and his collaborators.

3.3 Thermal properties of the PAIs

The thermal properties of the PAIs were evaluated by DSC and TGA/DSC in a nitrogen atmosphere, as it can be seen in the data summarized in Table 5. The incorporation of amide groups along the chain tend to increase PAI processing because its chemical structure allows mobility, free rotation and, therefore, flexibility. The parameter used to analyze this effect is the glass transition temperature (T_g) determined by DSC (Fig. 4), when its value decreases the polymer backbone flexibility increases. For this reason, *PAI*-1 shows the lowest value of T_g, due to the greater distribution of arrangements AA (amide-amide). Thus, the order of

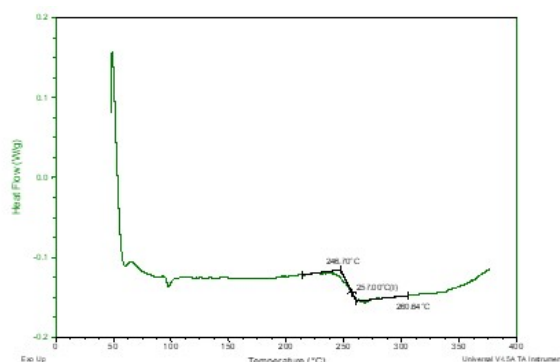processing is *PAI*-1>*PAI*-3>*PAI*-2 in relation to the increment of T_g.

Fig. 4. DSC thermogram of *PAI*-1 in nitrogen at a heating rate, 15 °C min^{-1}.
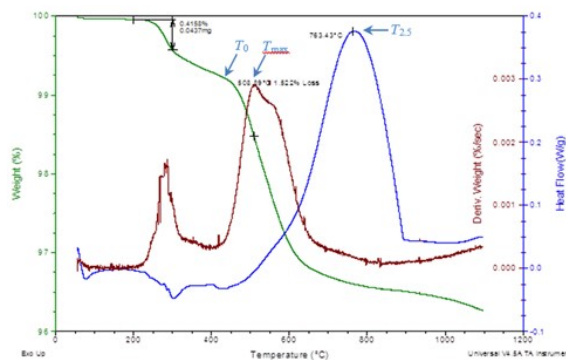

Fig. 5 TGA/DSC thermogram of *PAI*-1 in nitrogen at a heating rate, 10 °C min^{-1}.

Table 5. Thermal properties for the PAIs synthesized at 140 °C.

	T_0^a, °C	T_{max}^b, °C	$T_{2.5}^c$, °C	T_g^d, °C
PAI-1	410	508.9	763.4	257.0
PAI-2	420	519.8	770.3	292.7
PAI-3	415	512.6	767.8	280.4

[a] Onset temperature of weight loss rate determined by TGA/DSC

[b] Temperature of maximum weight loss rate determined by TGA/DSC.

[c] Temperatures at 2.5% weight loss

[d] Glass transition temperature determined by DSC of three runs.

When the distribution of arrangements II (imide-imide) increases the thermal stability is better. The parameters that allow to analyze this effect are onset temperature of weight loss rate (T_0), temperature of maximum weight loss rate (T_{max}) and 2.5% weight loss temperature ($T_{2.5}$), which were determined by TGA/DSC (Fig. 5 and Table 5). In thermograms are shown an initial percentage of weight loss of 0.42-0.46% at 200-250 °C due to loss of ocluded NMP. Subsequently, the PAIs exhibit excellent thermal stability showing values of T_0 from 410 to 420 °C and of T_{max} from 508.9 to 519.8 °C. The weight loss of 2.5% is observed from T_0 to $T_{2.5}$, when it is heated in a temperature range from 100 to 1100 °C. The 2.5% weight loss temperature ($T_{2.5}$) for *PAI*-1 was observed at 763.4 °C, for *PAI*-2 at 770 °C and for *PAI*-3 at 767.8 °C. The *PAI*-2 shows the highest values of T_0, T_{max} and $T_{2.5}$ due to a greater distribution of arrangements II (imide-imide). Thus, the order of thermal stability is *PAI*-2>*PAI*-3>*PAI*-1 in relation to the increment of T_0, T_{max} and $T_{2.5}$.

Conclusions

The chemical structure of the PAI was confirmed by techniques such as FTIR, ^{1}H-NMR and elemental analysis. The spectroscopic characterization confirms that the arrangement of groups AA (amide-amide), II (imide-imide) and AI (amide-imide) are random along the polymer chain. The result obtained by elemental analysis shows that the chemical composition corresponds to the chemical formula $C_{22}H_{14}N_2O_3$. The activation energy obtained by kinetic studies shows that the *PAI*-3 synthesis has a better experimental control, because the value is higher. Although ^{1}H-NMR spectra show arrangements

of groups AA, II and AI for all the PAIs regardless of the synthesis route, the thermal analysis studies indicate that there is a more likely distribution regarding the order of addition of reactants.

Nomenclature

PAI	polyamide imide
TMA	1,2,4-benzenetricarboxylic anhydride
MDI	diphenylmethylene diisocyanate
NMP	N-methyl-2-pyrrolidone
k	rate constant, $M^{-1} \cdot s^{-1}$
$-r_A$	reaction rate
n	reaction order
$[\eta]$	instantaneous intrinsic viscosity, $dL \cdot g^{-1}$
W	weight of PAI sample after being exposed to the environment
W_o	weight of PAI sample after dried in vacuum
DMF	dimethylformamide
$[A]$	concentration of the reagent

References

Aguilar, O.F., Vargas, R.O., Puing, J.E., Mendizábal, E., López, F. (2013). A simple proposal for modeling isothermal cure kinetics. *Revista Mexicana de Ingeniería Química 1*, 155-163.

Ambekar, A., Yoh, J.J. (2018). Chemical kinetics of multi-component pyrotechnics and mechanistic deconvolution of variable activation energy. *Proceedings of the combustion Institute 000*, 1-9.

Atanu, R., Yedidi, V., Vijay, K., Sukumar, M. (1983). Synthesis of polyamide-imides containing ether and sulfonamide groups. *Polymer Journal 15*, 169-173.

Ayala, J.A., Castillo, C.O., Ruis, R.S. (2017). Ultrasonic, ultraviolet, and hybrid catalytic processes for the degradation of rhodamine B

dye: decolorization kinetics. *Revista Mexicana de Ingeniería Química 2*, 521-529.

Biaobing, W., Meng, C., Guangming, L. (2016). Preparation method of conductive polyamide-polyimide composite. *CN 2016*-10908194.

Chatterjee, A., Maity, S. (2017). A comparative study of reaction kinetics of in-situ chemical polymerization of pyrrole onto various textile fibres. *Surface & Coating Technology 314*, 569-576.

Chen, L.W., Ho, K.S. (1996). Synthesis of polyamide-imide by blocked-methylene diisocyanates. *Journal of Polymer Science: Part A: Polymer Chemistry 35*, 1711-1717.

Chin-Ping, Y., Ruei-Shin, Ch. (1999) Preparation and characterization of colourless alternate poly(amide-imide)s based on trimellitic anhydride and m-phenylenediamine. *Polymer 40*, 1025-1034.

Correa, C., Tejeda, A., Martin, A.R., García, H.S., Noriega, J.A. (2017). Kinetics of the enzymatic esterification of n-3 polyunsaturated fatty acids to glycerol: multi-substrate multi-product ping-pong mechanism. *Revista Mexicana de Ingeniería Química 16*, 805-812.

Cuevas, C. (2006). Kinetics corrosion of ss-304 stainless steel exposed to a lithium bromide aqueous solution at low temperatures. *Revista Mexicana de Ingeniería Química 5*, 27-45.

Dollimore, D., Evans, T.A., Lee, Y.F., Pee, G.P., Wilburn, F.W. (1992). The significance of the onset and final temperatures in the kinetic analysis of TG curves. *Thermochimica Acta 196*, 255-265.

Domínguez, S., Domínguez, A., González, A., Navarro, S. (2007). Imbibition kinetics and moisture sorption isotherms of roselle seeds. *Revista Mexicana de Ingeniería Química 6*, 309-316.

Douglas, J., Garboczi, E. (2007). *Intrinsic Viscosity and the Polarizability of Particles Having a Wide Range of Shapes*. Editorial John Wiley & Sons Inc.

Fang, S., Wang, M., Xu, Z., Zhai, L., Wang, L., Xiong, Y. (2018). Preparation of an amphoteric flocculant having both high polymer content and

low viscosity and its polymerization kinetics. *Chinese Journal of Chemical Engineering*.

Félix, R.M., Heredia, M., Pérez, S., Salazar, M.I., Diaz, A.F., Lin, S.W. (2017). Kinetic parameter determination form MTBE degradation with persulfate and Ag$^+$ ions. *Revista Mexicana de Ingeniería Química 3*, 873-882.

Flowers, R.G., Sherer, T.L. (1975). Polyamide-imide compositions. US Patent 3862092. Haiyang Shi, Lei Zhang, Jinhai Cui. (2013). Study on of cure reaction kinetics of polyamide-imide epoxy resin. *Advanced Materials Research 746*, 128-131.

Ho, K.S., Chen, L.W. (1997) Kinetic Studies of Polyamide-imide Synthesis. *Journal of Polymer Science: Part A: Polymer Chemistry 35*, 1703-1710.

Holub, F.R., Scotia, N.Y. (1969). Aromatic polyimides. US Patent Office 3440215.

Holub, F.R., Cacciotti, P.J., Pauze, D.R. (1975). Polyamideimide compositions. US Patent Office 3922252.

Imai, Y., Maldar, N.N., Kakimoto, M. (1985). Synthesis and characterization of aromatic polyamide-imides from 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene and 4-choroformylphthalic anhydride. *Journal of Polymer Science 23*, 2077-2080.

Incremona, J., Strugar, D. (1974). Polyamide-imide polymer having an ordered structure. US Patent Office 3852106.

Izumi, M., Matsumura, S., Asano, N., Kawaguchi, M. (1974). Method for preparing soluble polyamideimides. US Patent Office 3803100.

Kikuchi, H., Hino, D., Takano, M., Funayama, H. (2011). Polyamde-mde resin based insulating varnish and insulated wire covered with same. US 0048766A1.

Levine, I.N. (2004). Fisicoquímica. Editorial McGraw-Hill Interamericana de España. López-Badillo M., Galicia-Aguilar J. A., Ortiz-Muñoz E., Hernández-Rodríguez G., Del Valle-Soto F. H. (2018). Chemical Cross-Linking of 6FDA-6FPA Polyimides for Gas Permeation Membranes. *International Journal of Chemical Reactor Engineering*.

Luna, K.Y., Arellano, S., García, S., Cornejo, M. (2017). Kinetic analysis of the stability of antioxidants in blackberry. *Revista Mexicana de Ingeniería Química 16*, 121-130.

Martínez, N., Antonio, R., Álvarez, A., Mendoza, A.M., Morales, A.B. (2007). Swelling kinetic of hydrogels from methyl cellulose and poly(acrylamide). *Revista Mexicana de Ingeniería Química 3*, 337-345.

Martinez, S.I. (2018). Analysis of thermoxidation kinetics of milk fat. *Revista Mexicana de Ingeniería Química 17*, 587-602.

Mehdi Barikani, Shahram Mehdipour Ataei. (1999). Preparation and properties of polyimides and polyamideimides from diisocyanates. *Journal of Polymer Science: Part A: Polymer Chemistry 37*, 2245-2250.

Meija, J., Coplen, T.B., Berglund, M., Brand, W.A., De Bièvre, P., Gröning, M., Holden, N.E., Irrgeher, J., Loss, R.D., Walczyk, T., Prohaska, T. (2016) Atomic weights of the elements 2013 (IUPAC Technical report). *Pure and Applied Chemistry 88*, 265-291.

Murray, T.J. (2008). Poly(amide-imides): Wire enamels with excellent thermal and chemical properties. *Macromolecular Material Engineering 293*, 350-360.

Navarro, R.S., Soto, S., Contreras, I., Piña, P., Viveros, T., Cuevas, E.O., Nieves, M. (2017). Effects of temperature and nitrogen limitation on growth kinetics, proximate composition and fatty acid profile. *Revista Mexicana de Ingeniería Química 16*, 359-369.

Ruiz, P., Guatemala, G., Mondragón, P.M., Zuñiga, E.A., Corona, R.I., Arriola, G. (2019). Empirical model of the chlorogenic acid degradation kinetics during coffee roasting in a spouted bed. *Revista Mexicana de Ingeniería Química 18*, 387-396.

Saotome, Takehiko. (2012). Aqueous polyamide-imide varnishes containing basic compounds and water, and coating materials containing them. *JP 2012*-134729.

Shen Chou, Ker-Sen Lee. (2002). A Study of polyamide-imide resin / copper foil composite materials. *Polymer Composites 11*, 57-68.

Shunchang, G., Kaikai, C., Jingmin, G. (2018). Polyamide imide and its preparation method. *CN 2018*-11513464.

Sintès, N., Pham, Q.T., Michaud, P. (1993). Low-molecular-weight poly(imide-amide)s obtained by copolycondensation of 4,4'-methylenedi(phenyl isocyanate), trimellitic acid anhydride and benzoic acid in N-methyl-2-pyrrolidone, 1. *Macromolecular Chemistry 194*, 2295-2307.

Solís, A., Rivas, P., Escamilla, C., Rico, R., Bravo, M.G., Botello, J.E. (2017). Methanol production kinetics during agave cooking for mezcal industry. *Revista Mexicana de Ingeniería Química 3*, 827-834.

Solomon, O., Ciuta, I. (1962). Détermination de la viscosité intrinsèque de solutions de polymères par une simple détermination de la viscosité. *Journal of Applied Polymer Science 6*, 683-686.

Takuya, K., Toshihiro, A. (2010). Polyimide-imides soluble in low-boiling point solvents and their ink materials and inks. *JP 2010-144109*.

Yang Tan, Khashayar Ghandi. (2013). Kinetics and mechanism of pyrrole chemical polymerization. *Synthetic metals 175*, 183-191.

Yuhong-Qia, Bingnan-Ji, Li-Li, Zhanping-Zhang. (2017). Synthesis and curing process of TMA-MDI polyamide-imides. *MATEC Web of Conferences 130*, 07007. DOI:10.1051/matecconf/201713007007

Zecher, W., Merten, R. (1969). Process for the production of polyamide imides by reacting polycarbonamide with aliphatic diisocyanate and cyclic dicarboxylic acid anhydride. US Patent Office 3752791.