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Laurent Verny, Noellie Ylla, Fernande da Cruz-Boisson, Éliane Espuche, Régis Mercier, et al.. Solvent-Free Reactive Extrusion As an Innovative and Efficient Process for the Synthesis of Polyimides. Industrial and engineering chemistry research, 2020, 59 (37), pp.16191-16204. 10.1021/acs.iecr.0c02881 . hal-03007653

HAL Id: hal-03007653

<https://hal.science/hal-03007653>

Submitted on 6 Jan 2021

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Solvent-free reactive extrusion as an innovative and efficient process for the synthesis of polyimides

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Abstract

Polyimides are commonly synthesized in a 2-step solution polymerization process. Such process requires long reaction times as well as specific care due to the use of potentially harmful solvents. In the present study, the total reaction time for producing polyimides has been lowered to less than 10 min by using a solvent-free continuous reactive extrusion process. The proof of concept was determined with the system based on 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) and an aliphatic diamine, Jeffamine D-230 within a micro-extruder. Conversion degrees to polyimide, determined with ^{13}C NMR and DSC analysis, are over 90 mol% after 5 min of extrusion at 180 °C, 200 °C and 225 °C respectively. These syntheses were then transferred to a twin-screw extruder to form linear aliphatic-aromatic polyimides with two types of dianhydride: BTDA and pyromellitic dianhydride (PMDA). Comparison with a conventional solution polymerization process showed no significant differences in the polymers characteristics. The polyimides produced with this method presented glass transition temperatures ranging from 5 to 90 °C. The number average molar masses measured were between 11000 and 15000 g.mol⁻¹.

Keywords: solvent free synthesis; thermal imidization; partially aliphatic polyimide; reactive extrusion

1 Introduction

Polyimides (PI) are a class of high-performance polymers, well-known for their outstanding chemical and thermal stabilities, as well as for their high mechanical properties. Examples of commercially available polyimides include DuPont's Kapton[®] and Vespel[®], Saint Gobain's Meldin[®] or UBE's Upilex[®]. Because of their exceptional properties, polyimides are mainly used in high-end applications, for which the cost factor does not drive the selection of the materials¹⁻³. One of the most famous applications is the multilayer insulation used for aerospace radiative protection (e.g. on satellites), identifiable by the “golden” aspect of the material⁴. Polyimides are widely used as gas separation membranes⁵⁻⁶ and are also investigated for the manufacturing of polymer electrolyte membrane fuel cells (PEMFC)⁷⁻¹⁰. More common applications are related with their mechanical and electric insulation properties: for instance polyimides are often used in the wiring insulation of laptop computers¹⁻⁴.

The polyimide synthesis was first described by Bogert in 1908, where 4-aminophthalic acid is first heated and dried to form 4-aminophthalic anhydride. The thermal treatment of the anhydride leads to the formation of a “polymolecular imide”, as written by the authors¹¹. However, the most common way to synthesize polyimides consists of the polycondensation reaction of diamine and dianhydride monomers in solution.

The reaction is generally achieved in two steps. First, an intermediate poly(amic acid) (PAA) is formed, which is then cyclized into polyimide (imidization reaction) upon heating in a range of temperatures between 100 °C and 300 °C, depending on the chemical structure. For this polymerization reaction performed in solution, high-boiling-point aprotic solvents – such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) or N,N-dimethylacetamide (DMAC) – are commonly used¹²⁻¹⁴. The preparation of polyimides

through solvent route is a straightforward process; however the total preparation time is long and comprises the formation of the PAA, the imidization reaction and the solvent removal (precipitation and filtering then vacuum drying, or solvent casting). The formation of the PAA lasts between 15 min (with LiCl to avoid charge transfer issues¹⁵) and 2 h¹⁶ at room temperature, but can be carried out for longer times to ensure complete conversion of the formulation. The thermal imidization reaction time ranges between few minutes (e.g. 15 min at 300 °C)¹⁷ and several hours (4 h at 160 °C)¹⁸. Besides, the chemical imidization reaction requires carboxylic dianhydrides as dehydrating agents and tertiary amines as catalysts. This second imidization route is described as allowing a better control of the reaction than thermal imidization. Furthermore, it can advantageously prevent the thermal degradation of the monomers and is subsequently carried out for thermally sensitive reagents^{19,20}.

In order to ensure fast synthesis of polyimides, some research works have reported the imidization into an extruder of a PAA oligomer obtained from the reaction of 4,4'-bisphenol A dianhydride (BPADA) with 1,3-phenylenediamine, carried out in dichlorobenzene. The temperature of the extrusion process is between 370 and 400 °C and the average molar masses of the resulting product are 20 000 g.mol⁻¹ and 50 000 g.mol⁻¹ for \overline{Mn} and \overline{Mw} , respectively. The drawbacks of this process are the solvent elimination during extrusion and the total reaction time: the solution polymerization of the PAA lasts 11 h prior to the extrusion. The residence time in the extrusion is very short (less than 2 min) and indicates that fast formation of polyimides could be achieved in specific conditions²¹.

The solution polymerization of polyimides requires the use of solvents that are now considered as hazardous chemicals or suspected to be carcinogenic, such as NMP. The solvent elimination step, carried out for both chemical and thermal imidization, requires the solvent to be disposed of, which can have a non-negligible impact on the environment. In a sustainable

environment approach, there is thus a real interest to develop alternative methods for preparing polyimides, and polymers in general, preventing the use of such solvents.

Early studies on the synthesis of polyimides described melt synthesis of the polymers as DuPont patent on the formation of poly(amide imide) fibers (PAI)²². Tri- and tetracarboxylic acids are used as reagents with primary diamines. The tetracarboxylic acid forms the imide moieties whereas the tricarboxylic acid leads to the amide part. The synthesis was carried out by melt process in a closed reactor heated at 200 °C. Similarly, Frosch's Bell patent²³ describes the formation of linear polyimides. However, the aliphatic structure of such polyimides cannot allow an injection molding process because of their poor thermomechanical stability, which subsequently limits their use as coatings or drawn fibers from the melt process.

Preparation of massive polyimide materials was described in Edwards' DuPont patents^{24,25} where the incorporation of aromatic structures in the dianhydride moieties and the use of "long" linear amine monomers offer the possibility of injection molding at 320 °C. The diamine and dianhydride reagents are first mixed together in a water/ethanol mixture leading to the formation of a prepolymer (PAA) that is under a salt form. Such process allows the PAA salt to be slightly soluble in water and requires no harmful solvents. The aqueous media is then heated over a few hours at 140 °C to progressively remove water, and then further treated at 280 °C (0.5 to 2 h) to complete the water removal and imidization reaction. The polyimides are then processed by injection molding into tubing for instance, and their glass transition temperature is claimed to be slightly over 100 °C, preventing the use of such polymers at high temperatures.

Fully aromatic polyimides have been investigated by Bower and Frost¹² and meet the requirements of high temperature materials; however, because of a lower alkaline activity of

the aromatic diamines, no salt of the PAA can be formed, forbidding the synthesis in water. Melt synthesis has been tested with aromatic reagents, but the fast hardening of the reaction media with the extent of the imidization decreases strongly the mobility of the diamine and dianhydride groups, leading to low molar mass polyimides. To solve this issue, the reaction was carried out in solution, so that high temperature materials could be produced. With the development of this process, the solvent-free approach has been progressively dropped out.

One way to produce “solvent-free” high temperature polyimides was to use slightly flexible monomers such as BPADA as patented by General Electric, and to form polyetherimide (PEI)²⁶⁻²⁸. In this process, the dianhydride and the diamine reagents are directly introduced in the extruder in which the imidization reaction is carried out. No solvent is needed with this technique; however very high temperatures are required to achieve the polymerization and to maintain the products in a molten state (300 to 350 °C).

More recently, Polyone Corporation patented a reactive extrusion process of imide oligomers made of asymmetric monomers, limiting the formation of charge transfer complexes. The extrusion is carried out at high temperatures, ranging from 320 to 370 °C. The average molar masses indicated in this patent are 10 000 g.mol⁻¹ and 16 000 g.mol⁻¹ for \overline{Mn} and \overline{Mw} , respectively²⁹. The products obtained are further used as thermosetting polymers for the manufacturing of composite materials. Cao et al³⁰ recently reported the synthesis of naphthalic imides and perylene diimides (PDIs): the PDIs were obtained by a continuous scalable solvent-free process using a twin screw extruder.

Thus, by using the extrusion synthesis, the total reaction time (between the introduction of the monomers and the obtaining of the final material) can be decreased to a few minutes of continuous process. This time-saving feature is an additional advantage for the polymer manufacturing.

Based on our expertise in both reactive extrusion and polyimide synthesis^{5,6,31,32} and being aware that, except for the patents detailed previously, no fundamental research work dealt with the synthesis of polyimide with this specific process, we thus studied different systems based on 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) as dianhydride reagents and Jeffamine D-230 as aliphatic diamine reagent. The aliphatic diamine was chosen in order to bring some flexibility to the polyimide chains and thus allowing extrusion temperatures around 200 °C. The corresponding polyimides were also synthesized for the first time by solution polymerization (microwave heating) as reference. Preliminary trials and kinetics measurements were performed on the BTDA/D-230 system at the laboratory scale with the use of a micro-extruder. The scaling up of this process was carried out using a twin-screw extruder with an estimated residence time between 4 and 7 min.

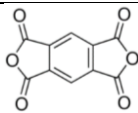
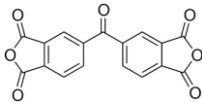
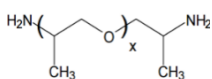
The chemical structure of the polyimides was investigated by FTIR and ¹³C NMR spectroscopies. The imidization reaction kinetics was determined using ¹³C NMR quantification and DSC analyses. The average molar masses, the glass transition temperatures and the thermal behavior were additionally characterized to fully describe the obtained polyimides.

2 Experimental

2.1 Materials

1,2,4,5-benzene tetracarboxylic dianhydride or pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) were purchased from Sigma-Aldrich and Abcr GmbH, respectively. Jeffamine D-230 was kindly provided by Huntsman. The structure and characteristics of the monomers are reported in **Table 1**. All the monomers were used as received.

Table 1: Chemical structures and characteristics of the monomers (dianhydrides and diamine)

Reagent	Abbreviation	Structure	M (g.mol ⁻¹)	Melting point (°C)	Boiling point (°C)
Pyromellitic dianhydride	PMDA		218.12	285	-
3,3',4,4'-benzophenone-tetracarboxylic dianhydride	BTDA		322.23	220	-
Jeffamine D- 230	D-230 (x=2.5)*		230**	-	232

* Technical sales specifications; ** number average molar mass

2.2 Synthesis of polyimides

2.2.1 Two-step micro-extrusion process

The samples were prepared with an Xplore DSM vertical micro-compounder (15 cm³ capacity) with double intermeshing counter-rotating screws. A manual floodgate, allowing either extrusion or recirculation, was used to carry out the reactive extrusion. Nitrogen inerting of the barrel was used.

a. Preparation of poly(amic acid)

Based on an equimolar ratio of BTDA and D-230, the poly(amic acid) (PAA) was obtained by blending 7 g of dianhydride (21.7 mmol) powder and 5 g of liquid diamine (21.7mmol) at ambient temperature for 5 min.

b. Imidization

The solid-like PAA was then introduced in the micro-extruder. The screws rotation speed was fixed at 50 rpm. Three processing temperatures were tested: 180 °C, 200 °C and 225 °C. Samples of reaction medium were collected at different extrusion time for further analysis.

2.2.2 Single step extrusion process

The device used was a Leistritz ZSE18 (60 L/D) co-rotating twin-screw extruder (represented in **Figure 1**).

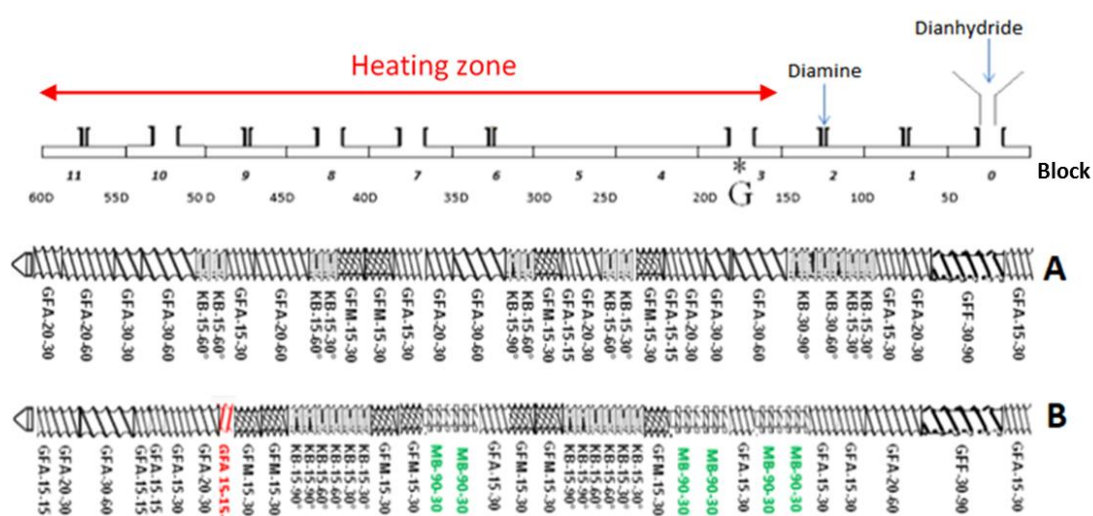


Figure 1: Representation of the twin-screw extrusion setup with the corresponding screw profiles (A and B)

Two different screw profiles were used. Screw profile B was set up to improve the mixing process for our formulations by multiple step by step modifications. Going from screw profile A to screw profile B, it can be observed that transporting elements were added in the early stages of the reactive extrusion (block 2) to limit the risk of clogging: during the formation of the PAA, the mixture of the reagents is difficult to process because of the high compact structure of the media²¹. The kneading blocks (KB) were moved towards blocks 4 and 5, and mixing blocks (MB) have been inserted in the screw profile to ensure a good homogenization of the PAA mixture. A counter-screw element was inserted in the late extrusion stage (block

9) to locally create a plug of polymer that will facilitate the elimination by vacuum extraction of the water formed upon imidization.

First, the dianhydride reagent is introduced at block 0 with a Brabender twin-screw gravimetric feeder. The feeding rate of dianhydride is 500 g.h^{-1} (1.55 mol.h^{-1} of BTDA or 2.29 mol.h^{-1} of PMDA). The diamine monomer (liquid at ambient temperature) is injected with an HPLC pump at the block 2. The diamine feeding rate is adjusted in order to get equimolar ratio of the two monomers.

Three extrusion temperatures (180, 200 or 225 °C) of blocks 3 to 11 were tested. The residence time in the extruder was estimated between 4 to 7 minutes (slightly higher for the screw profile B). The synthesized polymers obtained at the die of the extruder are further analyzed.

2.2.3 Solution process

In a PTFE vessel, 3.77 g of reagents (equimolar amounts of diamine and dianhydride) were solubilized in 21 mL of dimethylacetamide. The solution was then placed under microwave irradiation at 500 W for 15 min (the medium temperature was measured at 200°C)³³. The polymer was precipitated by pouring the reaction mixture into water. The polymer powder was recovered by filtration. It was then washed with water and finally dried for 24 h at 50 °C under vacuum. Two different polymers BTDA/D-230 and PMDA/D-230 were synthesized.

2.3 Methods of characterization

FT-IR spectra ranging from 650 to 4000 cm^{-1} were recorded using a Nicolet iS10 in attenuated total reflectance (ATR) mode (16 scans). The samples were directly analyzed in the solid state.

^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance II spectrometer working at 100.6 MHz for ^{13}C . The samples were dissolved in deuterated DMSO. Quantitative analyses were carried out with inverse gated proton decoupling (6k scans) to avoid Nuclear Overhauser Effect (NOE), a 70° rf pulse and 11.4 s recycle delay was used to allow complete relaxation of the carbons between each scan. Others samples were also qualitatively analyzed with power gated proton decoupling (3k scans), a 70° rf pulse and 4.4 s recycle delay.

Thermal properties (glass transition temperature T_g , residual reaction endotherm) were obtained from a TA Instruments DSC Q2000 under helium atmosphere. The runs were made with first a cooling step from 25 to -20 °C at 20 °C.min⁻¹, then a heating step to 250 °C at 10 °C.min⁻¹, followed by a another cooling step down to 25 °C. A second identical heating cycle was carried out to determine the T_g value.

Thermal stability properties of polymers were obtained from a TA Instruments TGA Q500 under helium atmosphere. The samples were heated from 25 °C to 550 °C at 10 °C.min⁻¹.

Size exclusion chromatography (SEC) measurements were carried out in DMF-LiBr (0.05 M) using an Agilent PolarGel L column. A Waters 2410 refractive index detector was used. Number average molar mass (\overline{M}_n) and mass average molar mass (\overline{M}_w) were calculated based on conventional calibration curve. The average molar masses are relative to polystyrene standards.

3. Results and discussion

3.1 Micro-extrusion trials

Addition of a dianhydride to a diamine at ambient temperature leads to the formation of the intermediate poly(amic acid), PAA (as checked by FT-IR and discussed in the next part), due to the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group.

This reaction, obtained by the dispersion of the solid dianhydride in the liquid diamine, is exothermic and the magnitude of the exotherm depends on the dianhydride and the diamine nature^{34,35}.

Moreover, the samples obtained after the synthesis step in the micro-extruder are all amber glass-like materials with physical properties and behavior depending on the formulation and reaction time. This color classically observed as a polyimide characteristic is already an encouraging signature of the formation of a polyimide through this reactive process. The proof of concept by micro-extruder was carried out with one system based on BTDA/D-230 and was extended to another system in the extrusion part to modulate the final properties.

3.1.1 FT-IR characterization

FT-IR spectra and characteristic frequencies of the BTDA/D-230 based polymers prepared at 200 °C versus residence time into the micro-extruder are plotted in **Figure 2**. This figure also displays the spectra of the polyimide prepared in solution and the reactional medium before introduction in the micro-extruder, supposed to be mainly composed of PAA. Assignments were made according to existing literature³⁶⁻³⁹.

PAA shows a characteristic broad signal near 1560 cm⁻¹ due to -C-NH- stretching of amide acid groups. The amide -C=O stretching resonance (near 1660 cm⁻¹) is overlapped with the ketone stretching of the BTDA⁴⁰. The 1850 cm⁻¹, 1780 cm⁻¹ and 1220 cm⁻¹ signals are characteristic of the cyclic anhydride vibrations^{36,37}, which demonstrates that the reactional mixture obtained at room temperature with BTDA and D-230 still contains unreacted anhydride. After barely 0.5 min of reaction at 200 °C, the FT-IR spectrum revealed the main polyimide characteristic absorptions such as the strong symmetric imide carbonyl stretching at 1710 cm⁻¹, the imide carbon-nitrogen stretching at 1370-1380 cm⁻¹ and the imide ring bending near 730 cm⁻¹³⁸. An additional weaker band at 1770 cm⁻¹ is due to the asymmetric imide

carbonyl stretching³⁹. Another strong absorption signal near 1100 cm^{-1} is the signature of ether bonds from the D230 diamine. The intensity of the 1560 cm^{-1} amide acid -C-NH- stretching broad signal decreases quickly in the early stages of the reaction (0.5 min), outlining a fast amide-acid cyclization process. The strong similarity of the FT-IR spectrum of the sample synthesized in solution with that of the sample obtained after an extrusion time equal to 4 min at 200 °C confirmed the fast imidization reaction by reactive extrusion.

To go further in the analysis of the polymers synthesized by reactive extrusion, the products obtained for the same reaction time of 0.5 min but at different extrusion temperatures are compared in **Figure 3**. The spectra are very similar to each other, and the only slight difference is by the 1560 cm^{-1} band (amide acid -C-NH- stretching): its absorption intensity is slightly higher for an extrusion temperature of 180 °C than for 200 °C, and is no longer present for 225 °C. This observation tends to confirm the swiftness of the imidization reaction and foreshadows faster reaction kinetics for higher temperatures.

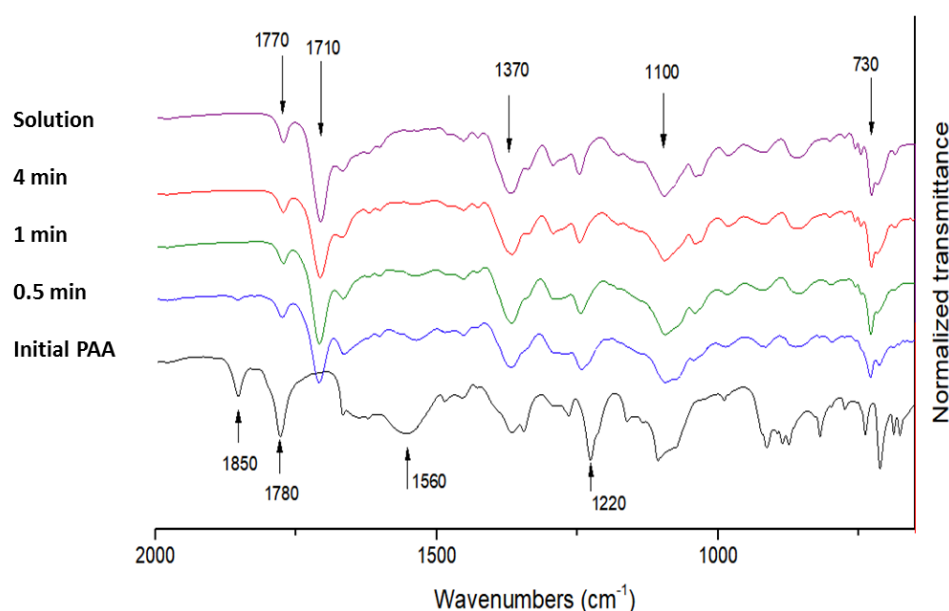


Figure 2: FT-IR spectra of BTDA/D-230 polyimides obtained in a micro-extruder at 200°C for different reaction times. Comparison with the spectra of the BTDA/D-230 polyimide obtained in solution and the corresponding initial reactive medium (mainly PAA).

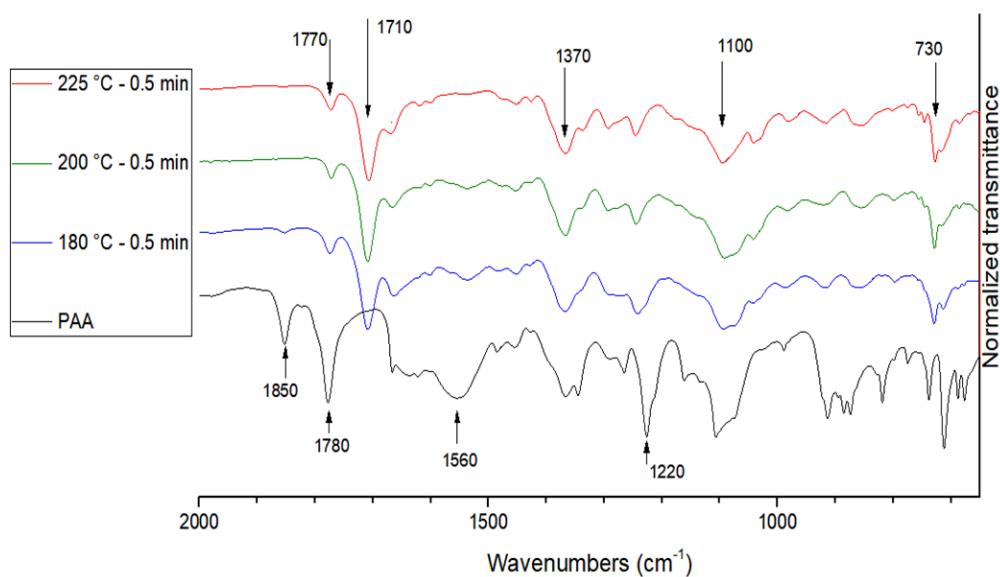


Figure 3: FT-IR spectra of the initial reactive medium mainly PAA (BTDA/D-230) and the corresponding polyimides obtained at 180 °C, 200 °C and 225 °C in a micro-extruder for 0.5 min reaction time.

3.1.2 ^{13}C NMR characterization

The chemical shifts for the different compounds are given in **Table SI1**. The assignment of the signals for the monomers and polymers was realized according to literature data⁴⁰⁻⁴⁴. Chemical shift predictions from Advanced Chemistry Development (ACD/Labs) software were also helpful to refine the attribution of the PAA and polyimide signals⁴⁵. **Figure 4** shows the detailed carbon labelling on the molecular structures.

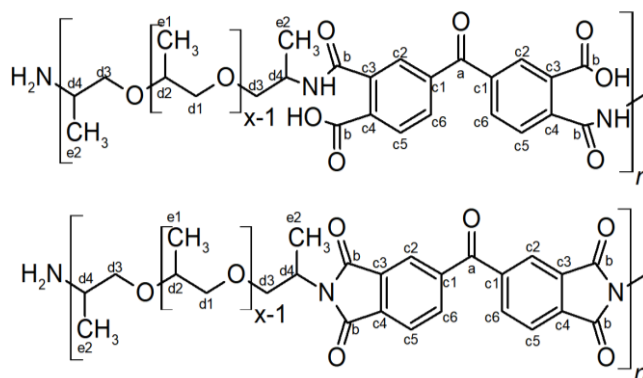


Figure 4: Structures and carbon identification for BTDA/D-230 poly(amic acid) and polyimide.

The ^{13}C NMR spectrum of the BTDA (not shown here, **Table SI1**) depicts a central ketone carbonyl (a, $\delta=193.9$ ppm) that is shielded by +1.17 ppm with the formation of the PAA (see **Figure 5**). The anhydride carbonyl signals b at 163.0 ppm are shielded towards a multiplet signal centered at 167.5 ppm with the formation of the PAA. Some of the aromatic signals (c_1 to c_6 , $\delta=120\text{-}150$ ppm) are also deshielded up to 4.6 ppm for the c_1 signal for example. A zoom of the carbonyl and aromatic signals region is displayed in **Figure 6**. BTDA-based poly(amic acids) can exist in 3 isomeric structures, plus 2 possible partially imidized forms, as shown in **Figure 7**. Such possibilities led to a visible multiplicity of the aromatic and carbonyl signals as it was studied by Ando *et al.*⁴⁶

On the ^{13}C NMR spectrum of a sample synthesized by micro-extrusion for 5 min at 200 °C, the signals are slightly enlarged which could be assigned to a change of structure/solubility. The multiple signal of the central ketone carbonyl (a) of the PAA is simplified to a single peak centered at 193.7 ppm after imidization. Imide carbonyl signal (b) also appears as a single signal at 167.7 ppm. The aromatic carbon multiple signals (c_1 to c_6) are also simplified to 5 different signals, one of them being twice more intense as the single other ones (c_2/c_5 , 123.9 ppm). Such simplification is due to the cyclization of the PAA isomeric functions to the single imide form. No common signals of the PAA functions are ever found in the spectra after a reaction time of 5 min in the micro-extruder.

For the PAA aliphatic signals (d to e), the amide/amine (d_4) signal is shielded by around -1 ppm, the methyl groups (e_1) are not affected by the reaction, and the e_2 signals are shielded towards the e_1 signals position.

For the polyimides obtained after a reaction time of 5 min at 200 °C in the micro-extruder, the e_2 signals are shielded by -2.3 ppm with the D-230 while the methyl group signal (e_1) remains unchanged. An interesting evolution concerns the d_4 amide/imide signal; the amide

acid CH resonance is located between 45.0 and 45.8 ppm, while the imide CH signal is shifted towards 46.5 to 47.5 ppm. This evolution will be exploited in the next section to measure the reaction kinetics.

For all the samples prepared by micro-extrusion, we can confirm that the imidization reaction of PAA can be completed in short reaction times. As a matter of fact, no residual PAA signals could be spotted in the ^{13}C NMR spectra of the polyimides obtained after a reaction time of 5 min at 200 °C in the micro-extruder.

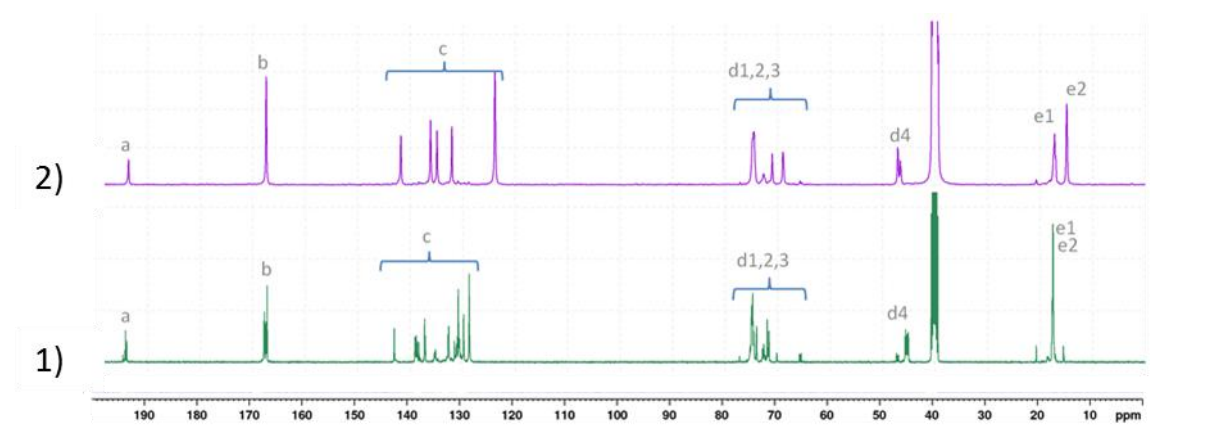


Figure 5: ^{13}C NMR Spectra (DMSO- d_6 , 25°C) of the initial reactive medium (mainly PAA from BTDA/D-230) (1) and BTDA/D-230 fully cyclized polyimide (micro-extrusion at 200 °C- 5 min) (2)

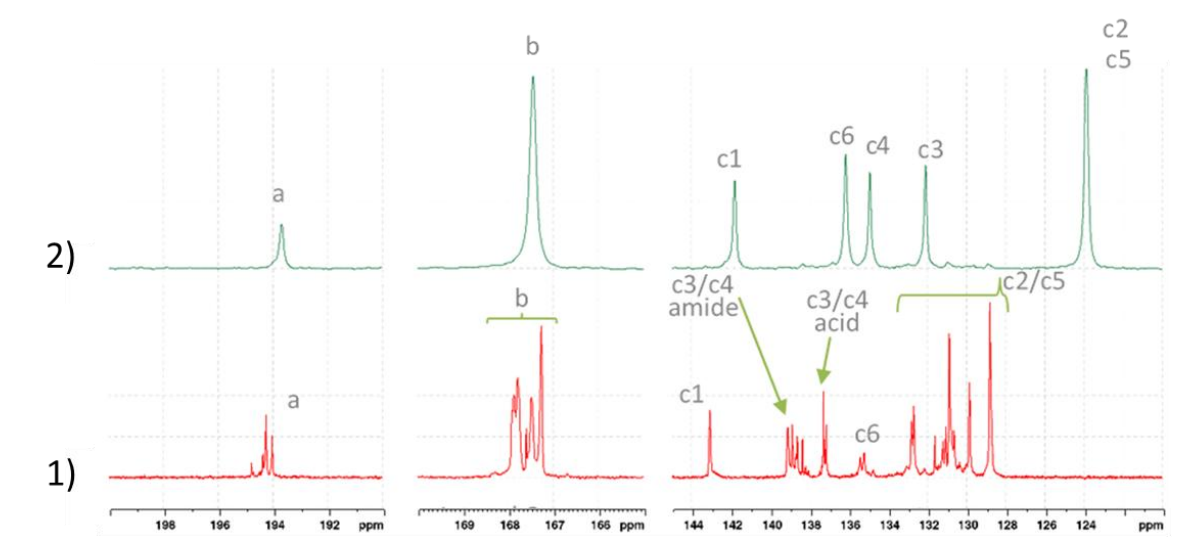


Figure 6: Zoom of the ^{13}C NMR Spectra (DMSO- d_6 , 25°C) of the initial reactive medium (mainly PAA from BTDA/D-230) (1) and BTDA/D-230 fully cyclized polyimide (micro-extrusion at 200 °C- 5 min) (2)

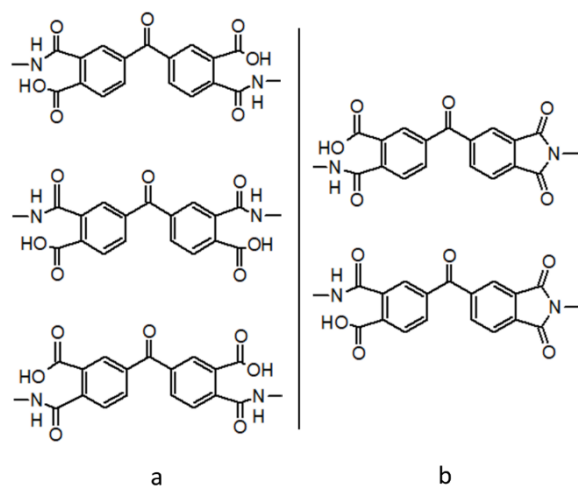


Figure 7: Structures of BTDA-based poly(amic acids) a: poly(amic acid) isomers b: partially imidized poly(amic acid) isomers

3.1.3 Imidization kinetics

The kinetics of the thermal imidization have been widely studied with various techniques⁴⁷, such as Fourier-transform infrared spectroscopy (FT-IR)⁴⁸, carbon-13 nuclear magnetic resonance (¹³C-NMR)⁴⁹ and ultraviolet-visible spectroscopy (UV-vis)³⁸. The imidization of PAA is an endothermic process that can be also monitored by differential scanning calorimetry (DSC)³⁹.

Polyimide conversion was calculated first from ¹³C-NMR. As shown in **Figure 8**, the CH d4 amide/imide signal is significantly shifted as the reaction occurs. The area of this specific signal can thus provide an accurate measurement of the imidization rate. The method used here is similar to the one used by Seshadri et al.⁴². The imidization rate α is given by the following formula (**Equation 1**):

$$\alpha \text{ (mol\%)} = \frac{\text{Area of imide d4 signal} \times 100}{\text{Total area of d4 signal (amic acid + imide)}} \quad (\text{Equation 1})$$

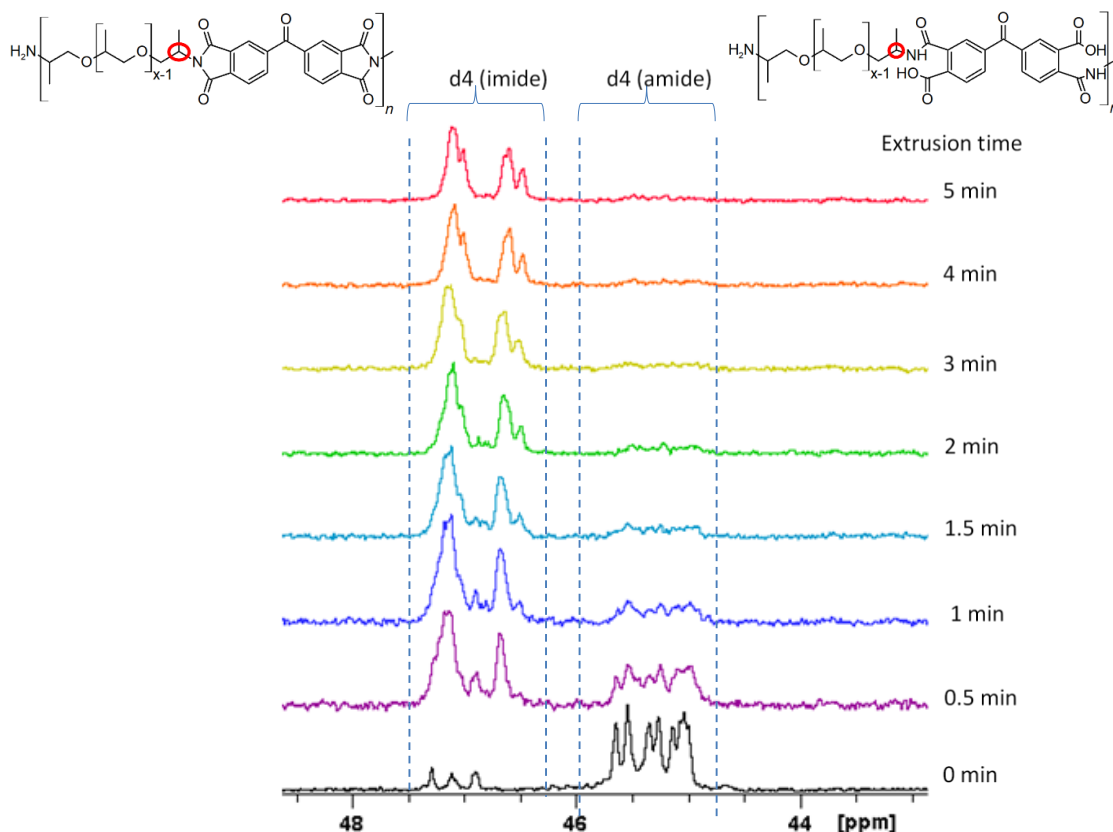


Figure 8: Evolution of the ^{13}C -NMR d4 signal of BTDA/D-230 reaction mixture (180 °C) alongside the extrusion time. The d4 carbon atom is circled in red on the chemical structures above (left: polyimide; right: poly(amic acid)). $t = 0$ min corresponds to the initial reactive medium (mainly PAA from BTDA/D-230)

Sampling of the reaction mixture during the micro-extrusion allowed us to build the kinetics of the polyimide cyclization. The corresponding conversion rates, obtained by this method for BTDA/D-230 system versus reaction time for different extrusion temperatures, are presented in **Table S 2** and plotted in **Figure 9**.

It has to be noticed that although the quantifications were mainly based on qualitative ^{13}C NMR analyses, they can be considered very accurate. Indeed, for the experiments carried out on the BTDA/D-230 system at 180 °C, we compared the spectra obtained through qualitative and quantitative conditions (detailed in experimental part). For those samples, no significant difference in relative integrals for the carbons of interest, meaning CH (d4) of PAA and polyimide, was observed for acquisitions made under those two conditions.

Note that some imide characteristic signals are already visible in the spectrum corresponding to the initial reaction medium (**Figure 8**). This observation is due to the fact that as soon as the dianhydride and the Jeffamine are put into contact at room temperature before their introduction in the micro-extruder, an exothermic phenomenon is observed coming from the amide-acid formation. The corresponding local increase of the temperature can lead to some parts of cyclization reaction to imide formation.

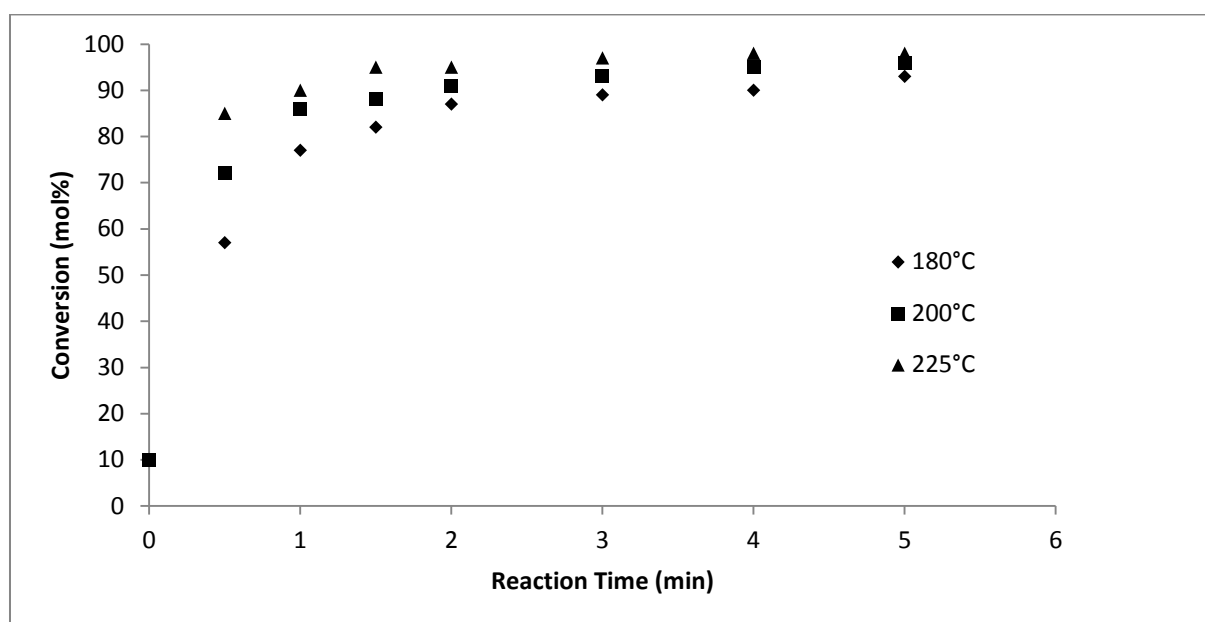


Figure 9: Imidization conversion curves over reaction time for BTDA/D-230 based polyimide systems synthesized in the micro-extruder for three different temperatures.

With this method, we confirm that the imidization for the BTDA/D-230 is very fast in the studied range of temperatures (between 180 and 225 °C) through a continuous extrusion process. An imidization conversion above 90 mol % after 4 min at 200 °C is specially promising for the scaling up part, where the residence time in our extruder is estimated between 4 and 7 min. Based on this result, it is expected to reach complete cyclization by using a twin-screw extrusion process.

As a complementary approach, the imidization reaction was also monitored by DSC analysis. Actually, as previously studied by Schab-Balcerzak et al.³⁹, the imidization process has been observed between 100 and 220 °C through the endotherm associated to the amide-acid cyclization reaction. The enthalpy measured for the initial PAA sample is considered as a reference of a “0 %” conversion rate.

For a given formulation, the imidization enthalpy decreases versus reaction time for a given temperature (**Figure 10**) and versus temperature for the same reaction time. As an example, the cyclization enthalpy values for BTDA/D-230 polyimide obtained at 180 °C are 37.1 kJ.mol⁻¹, 17.1 kJ.mol⁻¹ and 10.2 kJ.mol⁻¹ for 0.5, 2.5 and 4 min of reaction, respectively. As a reference, the imidization enthalpy value obtained for the initial PAA is 149 kJ.mol⁻¹.

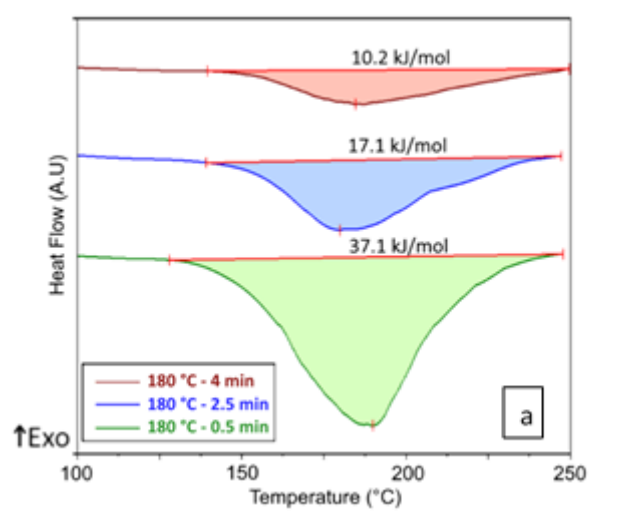


Figure 10: Evolution of the imidization endotherm intensity versus reaction times for the BTDA/D-230 system treated at 180°C

Our value agrees with literature data. The imidization enthalpy is 50.1 kJ.mol⁻¹ for PMDA/ODA (Anthamatten³⁶), 87.4 kJ.mol⁻¹ for PMDA/ODA (Belina⁵⁰), and 93.6 kJ.mol⁻¹ for PMDA/Benzidine (Chang⁵¹).

Subsequently, we determined the conversion rate by DSC with the following formula (**Equation 2**):

$$\text{Imidization rate (mol \%)} = \frac{\Delta H_{\text{sample}}}{\Delta H_{\text{polyamic acid}}} \times 100 \text{ (Equation 2)}$$

The results are shown in **Table S 3** and plotted in **Figure 11**.

The DSC measurements confirm the results obtained by ^{13}C -NMR: the imidization of our formulations in a micro-extruder is a fast process that can reach high conversion rates. The measured conversion rates are in the same range with both methods. An imidization rate over 90% can be achieved after 4 min of reaction for the temperatures investigated (180, 200 and 225 °C).

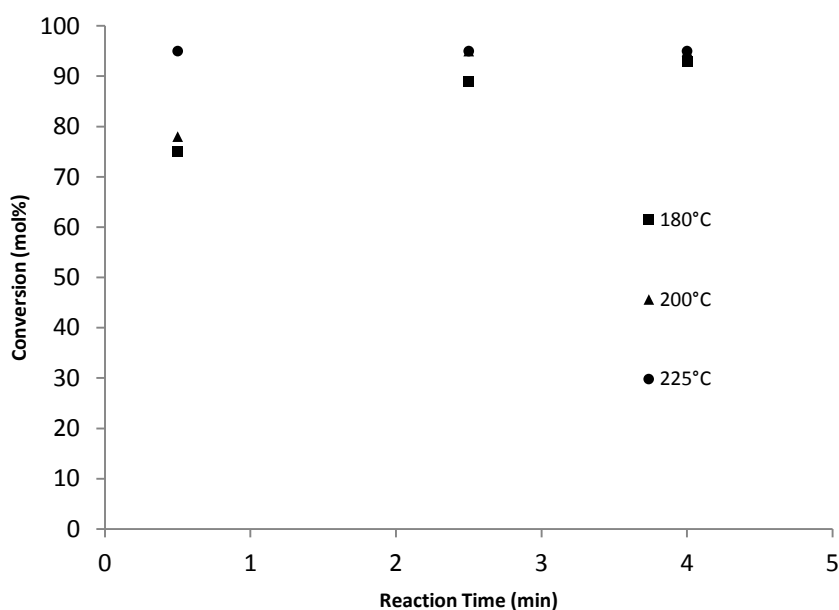


Figure 11: Imidization conversion rate over time for BTDA/D-230 based polyimide systems synthesized in the micro-extruder for three different temperatures.

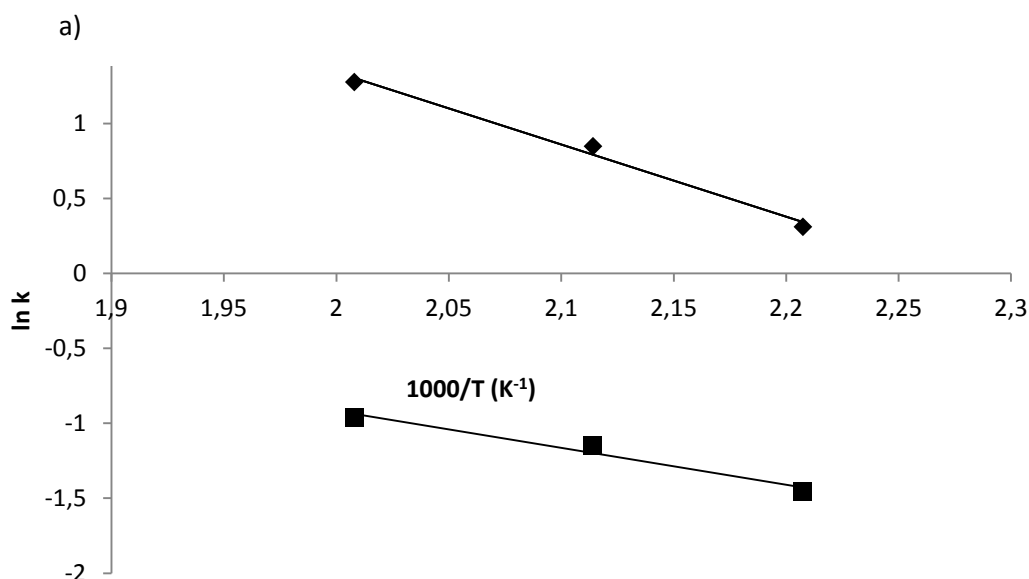
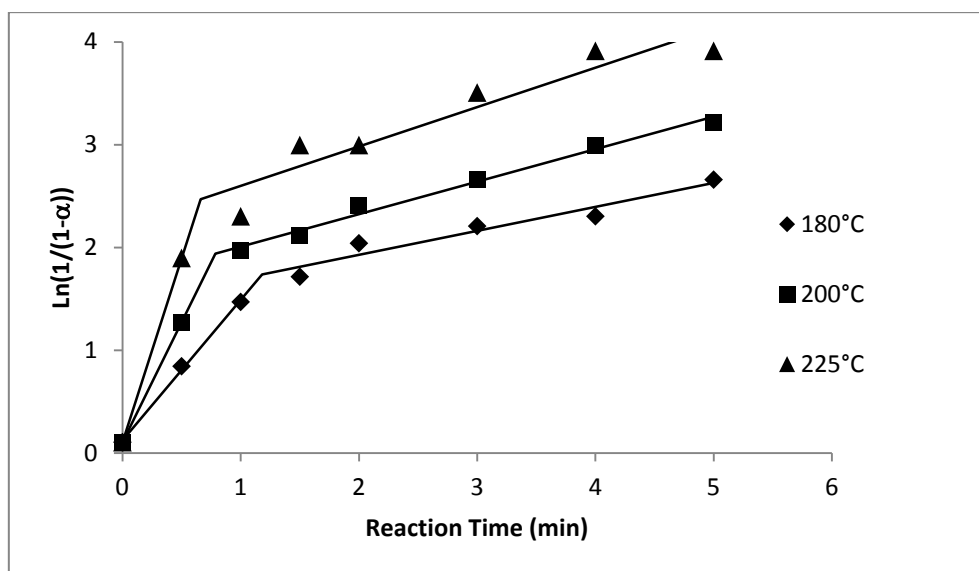
The imidization reaction involves an amide and a carboxylic acid group. As these two groups belong to the same chemical species, the authors^{38,49} classically consider the kinetics as a first order law expressed with the following rate expression (Equation 3):

$$\ln(1/(1 - \alpha)) = kt + \text{constant} \quad (\text{Equation 3})$$

where k is the rate constant, α the imidization reaction conversion and t the reaction time.

The plots of $\ln(1/(1-\alpha))$ as a function of the reaction time t at different temperatures for the BTDA/D-230 system is reported in **Figure 12a**). Note that these curves have been drawn from the ^{13}C NMR data (similar curves not shown here were obtained from the DSC data). From the analysis of these curves and their best fitting, it is clearly shown that whatever the temperature and the system considered, the imidization reaction proceeded via a two-step process. Actually, it is characterized by an initial rapid cyclization and a second slower cyclization mechanism. These observations are consistent with the numerous studies dealing with this subject⁵²⁻⁵⁴. In particular, most of the contributions dedicated to solid-state imidization reaction described these phenomena and proposed the following explanation. As the cyclization reaction proceeds in mass, the concentration of active amide-acid groups is decreasing concomitantly to a decrease of the molecular mobility in the polymer backbone. Moreover, others authors such as Pyun et al.³⁸ argued also an initial contribution of the catalytic effect of the amide acid groups on the kinetics which also decreases with the cyclization reaction conversion. Besides, from a quantitative approach, it is possible from these curves to extract two rate constants (k_1 for the initial fast step and k_2 for the slower one **Figure 12 b**)) and finally the activation energy of both reactional steps. Actually, the values k_1 for the fast step are comprised between 1.36 min^{-1} at 180°C and 3.58 min^{-1} at 225°C ; and the values of k_2 for the slow step are comprised between 0.23 min^{-1} at 180°C and 0.39 min^{-1} at 225°C . They are classically increased with the temperature and related to the modification of the molecular mobility (difference between k_1 and k_2). Concerning the activation energy, we respectively obtained 40.1 kJ.mol^{-1} for the faster reactional step and 20.4 kJ.mol^{-1} for the slower one. Such values are quite low in comparison with standard values given by previous studies (PMDA/ODA: $101.6 \text{ kJ.mol}^{-1}$ according to Seo⁵², 96.6 kJ.mol^{-1} according to

Tsapovetskii⁵⁵; 6FDA/diaminoazobenzene : 46 and 75 kJ.mol⁻¹ according to Pyun³⁸; BTDA/diaminonaphtalene 50.2 kJ.mol⁻¹ according to Jen⁵⁶). This can be explained by the very flexible structure of our polyimides due to the non-aromatic Jeffamine monomer, promoting the cyclization of the amide acid groups.



b)

Figure 12 : a) Kinetic plots of $\ln(1/(1 - \alpha))$ as function of time at different temperatures: (■) 180 °C; (●) 200 °C; (▲) 225 °C and b) the corresponding Arrhenius plot of $\ln k_1$ (fast step upper line) and $\ln k_2$ (slow step lower line) versus $1000/T$ for the BTDA/D-230 system. Lines provide the model calculations considering two first-order kinetics.

3.2 Reactive extrusion

Micro-extrusion results with the BDTA/D-230 system are very promising for the twin-screw extrusion transfer, especially regarding the conversion rate of PAA to polyimide, where nearly complete imidization could be achieved in a reaction time around 4-5 min. Adequate screw profiles were selected for the extrusion transfer, with a residence time comprised between 4 and 7 min.

We tested the synthesis of the BTDA/D-230 based polyimide but also enlarged our series to the PMDA/D-230 system and carried out the extrusion at 180, 200 and 225 °C.

First, we compared by FTIR the spectrum of the BTDA/D-230 based polyimide obtained with the micro-extruder after 5 min at 200 °C with the one of polyimide extruded at 200 °C with the screw profile B. The spectra of PAA and the corresponding polyimide obtained in solution are also reported in **Figure 13**.

The spectra of the polyimides prepared by the three methods at 200°C are similar with the same wavenumbers and relative intensities of the absorption bands. More specifically, the characteristic absorption bands of polyimides (1780 cm^{-1} and 1710 cm^{-1} imide carbonyl stretch; 1370 cm^{-1} imide -C-N- stretch; 730 cm^{-1} imide ring bending) are present in the spectra of the samples prepared by the three methods (**Figure 13**). Moreover, the absence of the -C-NH- stretching of amide acid groups (near 1560 cm^{-1}) confirms that all the amide acid groups were converted in imide groups during the extrusion.

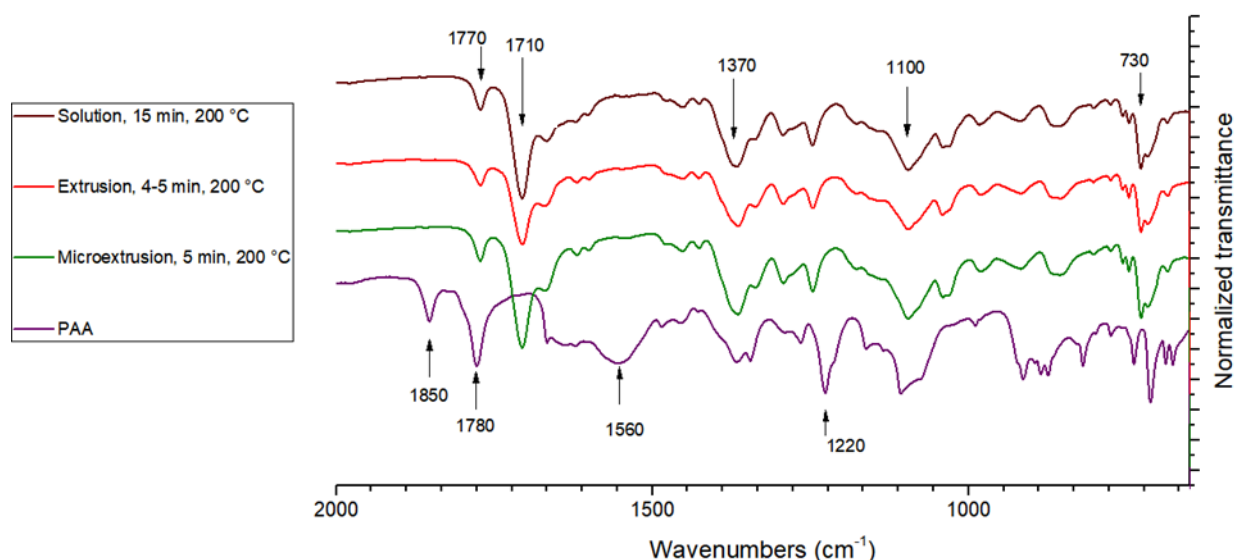


Figure 13: FT-IR spectra of the initial reactive medium mainly PAA (BTDA/D-230 molar ratio = 1) with the corresponding polyimide obtained by micro-extrusion, extrusion (screw profile B) and solution polymerization at 200 °C.

Similarly, the FTIR spectra of the PMDA/D-230 and BDTA/D-230 polyimides synthesized by extrusion at 180 °C, 200 °C and 225 °C were compared with the spectrum of the corresponding polyimide prepared in solution. As shown in **Figure 14** for the PMDA/D-230 system, the temperature has no incidence (for the studied range of residence time) on the resulting spectra for the polyimides prepared by extrusion. The polyimide characteristic bands (1780 cm^{-1} and 1710 cm^{-1} imide carbonyl stretch; 1350 cm^{-1} imide -C-N- stretch; 730 cm^{-1} imide ring bending) are similar in frequency and intensity. Moreover, the spectra of the polyimides synthesized by twin-screw extrusion are, for the three temperatures studied, similar to the one of the polyimide obtained by solution polymerization. These results evidence that the imidization reaction is successfully carried out with the extrusion process above 180 °C with the screw profile B.

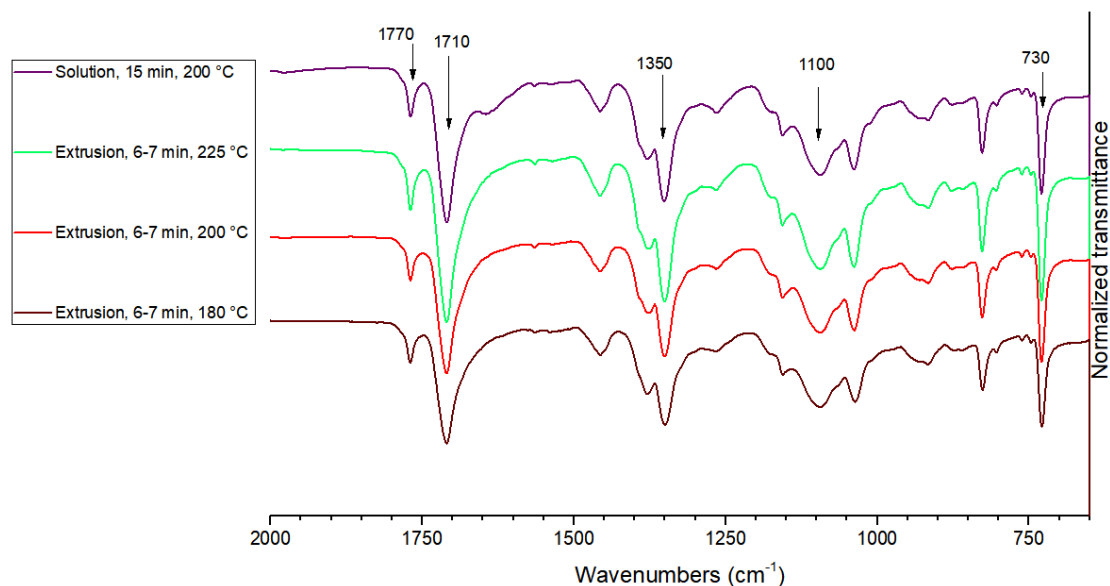


Figure 14: FT-IR spectra of PMDA/D-230 based polyimides obtained by extrusion performed at different temperatures (screw profile B) and solution polymerization carried out at 200°C.

These observations are confirmed by ^{13}C NMR, where the conversion rate was measured according to **Equation 1**. For both BTDA/D-230 and PMDA/D-230, the imidization rates are over 95%.

We observed that the screw profile does affect the imidization reaction during the extrusion process. For PMDA/D-230 polyimides prepared by extrusion at 200 °C with the screw profile A, we noticed a slight difference on the polyimide FTIR spectrum compared to the one obtained when using the screw profile B. As shown in **Figure 15**, samples prepared with the screw profile A exhibited absorption bands near 1850 cm^{-1} and 1785 cm^{-1} . These signals could be due to an excess of anhydride in the reaction media and the presence of unreacted anhydride or residual amide-acid groups.

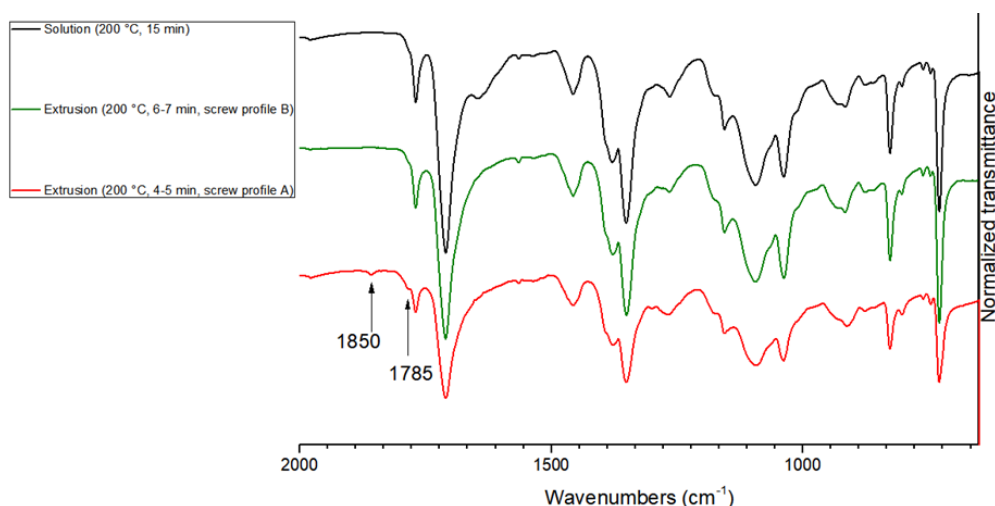


Figure 15: FT-IR spectra of PMDA/D-230 polyimides obtained by extrusion at 200°C with screw profiles A and B and the corresponding polyimide prepared by solution polymerization.

This observation evidences the importance of accurately controlling the molar ratio of the reagents alongside the extrusion process to avoid stoichiometry unbalancing but also to use the proper screw profile to enhance the reaction conversion. The optimization of the screw design towards the screw profile B, with the insertion of the kneading blocks (KB) and the mixing blocks (MB), improved the mixing of the reagents during the PAA formation, thus limiting the effects of local stoichiometry variations.

3.3 Specific properties

3.3.1 Average molar masses

First, we monitored the evolution of the molar mass versus time of micro-extrusion at 200 °C for the system BTDA/D-230. As displayed in **Figure 16**, the elution peak shifts toward lower elution volumes (i.e. higher molar masses) when the imidization reaction time increases. This variation is clearly related to the conversion of the amide-acid group to imide group (from 72 to 91 and 96 mol % as determined previously by ^{13}C NMR for 0.5, 2 and 5 min of microextrusion, respectively). Actually, as the molar mass is fixed as soon as the PAA is formed, this shift may be plausibly due to the potential interaction of residual amide-acid groups of the polymer with the stationary phase leading to a higher elution volume. This

hypothesis was already reported by several other authors even if the addition of LiBr should have limited/inhibited these interactions⁵⁷⁻⁵⁹. Besides, this observation may also be due to an evolution of the hydrodynamic volume of the polymer chains alongside the imidization reaction.

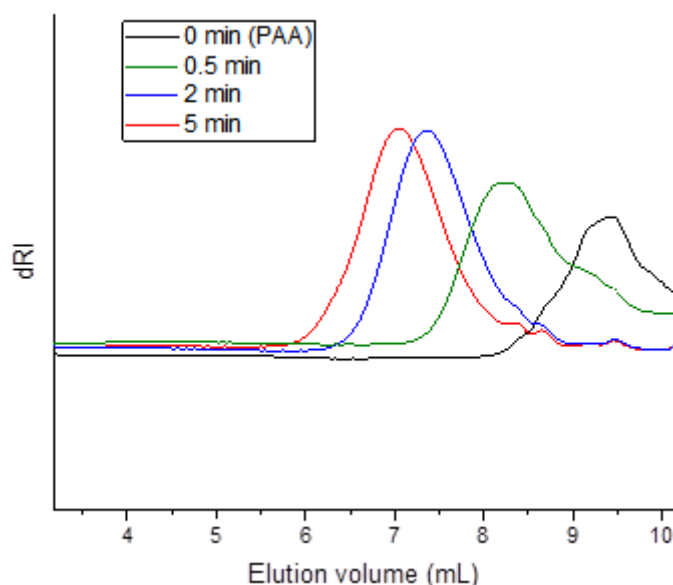


Figure 16: SEC curves for BTDA/D-230 based polyimides and corresponding initial reactive medium (mainly PAA). Polyimides were obtained by micro-extrusion at 200 °C for different reaction times.

Furthermore, the SEC results for the BTDA/D-230 samples obtained at 200 °C by micro-extrusion after 5 min of reaction time or by extrusion are compared to the average molar masses obtained for the reference synthesized in solution (**Table 4**). Some data for the PMDA/D-230 systems are also reported.

As it is clearly shown in this table, there is a good agreement between the average molar masses of the polyimides prepared at 200 °C with the different processes. For the BTDA/D-230 system, \overline{Mn} is between 11 000 and 15 000 g.mol⁻¹, while \overline{Mw} is between 24 000 and 45 000 g.mol⁻¹ (\overline{D} is between 2.1 and 3.1). The PMDA/D-230 system follows a similar trend. The solution polymerization process seems to allow a slightly narrower polydispersity of the polyimides chains with respect to the extrusion process. Once again, this information

confirmed the possibility to reach polyimide structures through a molten continuous process with molecular characteristics similar to the ones obtained in more usual solution-based chemistry, without solvent and with shorter reaction times.

Table 4: SEC values of BTDA/D-230 and PMDA/D-230 polyimides synthesized at 200 °C and analyzed in DMF-LiBr (10% uncertainty)

Polyimide	BTDA/D230			PMDA/D230	
Process	Micro-extrusion (5 minutes)	Extrusion	Solution	Extrusion	Solution
\overline{Mn} (g.mol ⁻¹)	11 000	14 750	13 500	13 350	10 900
\overline{Mw} (g.mol ⁻¹)	24 000	45 200	38 500	40 200	23 100
\overline{D}	2.2	3.1	2.8	3.0	2.1

3.3.2 Glass transition temperatures

The glass transition temperatures (T_g) of the obtained polyimides were determined by DSC analysis. The thermograms for BTDA/D-230 system are shown in **Figure 17** and the values for both BTDA/D-230 and PMDA/D-230 systems are reported in **Table 5**.

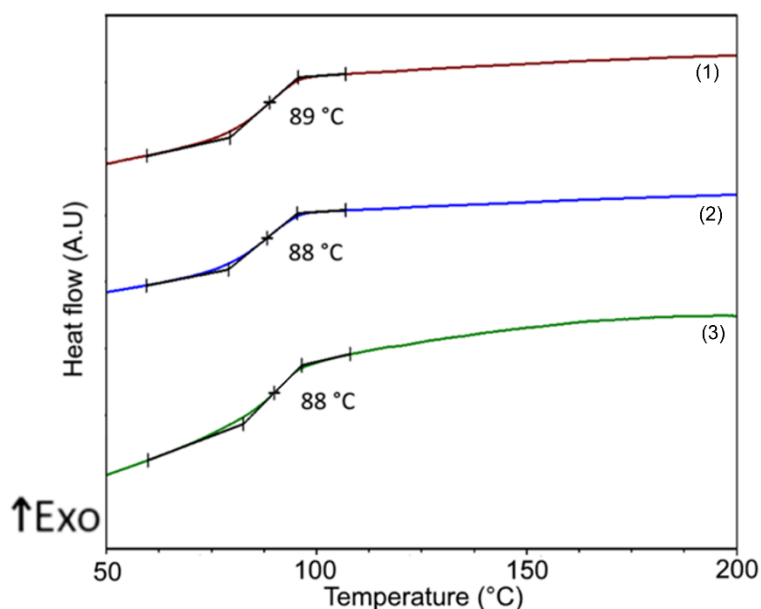


Figure 17: DSC thermograms of BTDA/D-230 polyimides prepared at 200 °C by extrusion (1), micro-extrusion (2) and solution polymerization (3).

Table 5: T_g values for polyimides obtained at 200 °C with different processes and measured by DSC analysis (uncertainty $\pm 1^\circ\text{C}$)

	Process	BTDA/D-230	PMDA/D-230
T_g (°C)	Micro-extrusion (5 min)	88	75
	Extrusion	89	71
	Solution	88	73

These data clearly evidenced that there are no major differences regarding the T_g of the samples prepared by micro-extrusion, twin-screw extrusion or solution polymerization for both dianhydride and D-230 diamine. These analyses confirm that the synthesis of polyimides by reactive extrusion leads to materials with thermal properties similar to those obtained by a more conventional solution polymerization route but with much shorter elaboration time.

The glass transition temperature values of the polyimides based on PMDA are substantially lower by 15 to 20 °C in comparison with BTDA-based polyimides despite comparable molar masses. This is quite surprising, since PMDA-based polyimides are known for presenting a higher T_g than BTDA-based polyimides for a given diamine. For instance, the T_g of a PMDA/ODA polyimide is over 380 °C, whereas the T_g of a BTDA/ODA polyimide is around 280 °C⁶⁰. However, this glass transition temperature can be reduced with the flexibility of the polymer chains. Eastmond et al.⁶¹, who synthesized polyimides by varying the number of ethylene oxide (EO) segments, showed that the glass transition temperature can range from 270 °C to sub-ambient temperature; for example, a T_g of 108 °C is found for a diamine with four EO sequence with ODA. This tendency, also observed with the D-230 diamine based structure, is thus consistent with the flexibility brought by the ethylene oxide segments⁶¹.

3.3.3 Thermal stability

All PDMA-based samples were analyzed by TGA under He atmosphere ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$). As depicted in **Figure 18**, the PMDA/D-230 polyimides remain stable under these dynamic conditions for temperatures up to $300\text{ }^{\circ}\text{C}$. Hence, the polyimides do not exhibit any significant mass drop at temperatures below $200\text{ }^{\circ}\text{C}$, except for the one obtained by solution polymerization. For this sample, the small weight loss (around 5wt%) observed at 200°C could be assigned to residual solvent. For the polyimides obtained by micro-extrusion or extrusion, no mass drop is evidenced at temperatures below 200°C which is consistent with a complete imidization reaction as no further water is formed. Over $350\text{ }^{\circ}\text{C}$, the samples then lose more than 85% of their original mass, and the residual char yield at $550\text{ }^{\circ}\text{C}$ is around 10%. The thermal behavior is very closed whatever the synthesis protocol confirming once again the similar properties of the polyimides synthesized either by solution or melt polymerization reaction. These thermal stabilities are lower to what is generally observed for aromatic polyimides, which are stable up to a temperature of $400\text{ }^{\circ}\text{C}$ under N_2 atmosphere. Again, the flexibility brought by the D-230 diamine impacts the thermal stability, but this property remains interesting for a large domain of applications. It has to be noted that similar trends as those observed for PMDA/D-230 polyimides were obtained for BTDA /D-230 polyimides with a degradation temperature around 320°C in this last case.

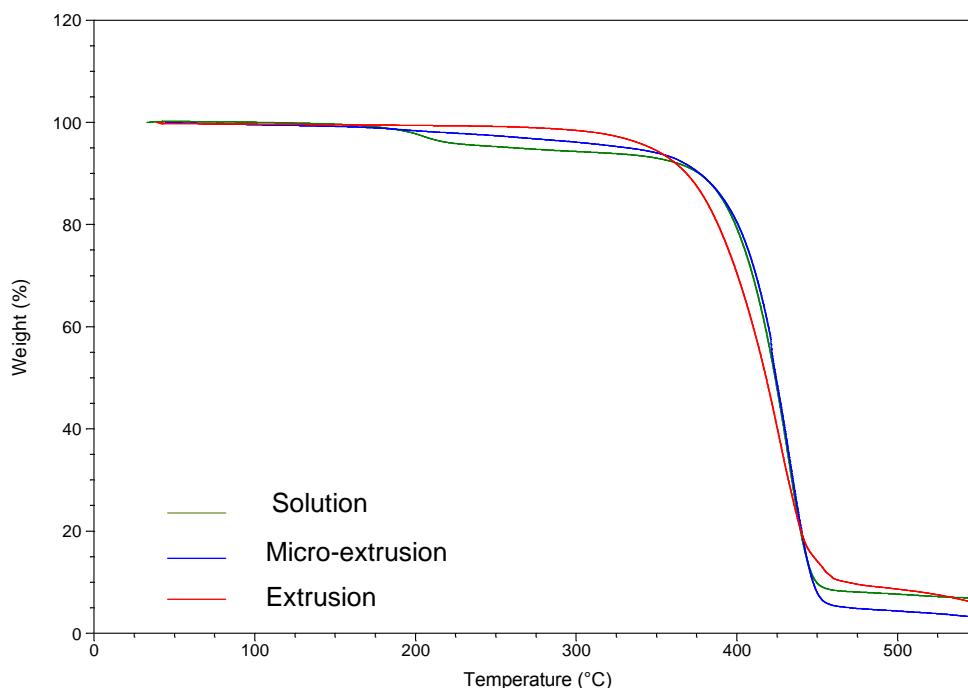


Figure 18: TGA analyses of PMDA/D-230 polyimides prepared at 200 °C by respectively extrusion, micro-extrusion and solution polymerization

4. Conclusion

Several polyimides based on PMDA or BTDA as dianhydride and Jeffamine D-230 as diamine have been synthesized through a molten process without solvent. First, the imidization reactions were carried out in a micro-extruder for the BTDA/D-230 mixture and the products obtained for different reaction times within the range (0-5 min) and for 3 temperatures (180°C, 200 and 225°C) were analyzed by FT-IR and ^{13}C -NMR spectroscopies. It was evidenced that a complete cyclization is reached in less than 5 min at 200 °C. A two-step imidization kinetics was proposed with an activation energy for the first fast reactional step of 40 kJ.mol⁻¹.

The synthesis was then scaled up for all the systems within a twin-screw extruder. Similarly, complete imidization could be achieved within 4 to 7 min of residence time at 200 °C. The polyimides synthesized by micro-extrusion, twin-screw extrusion and solution polymerization exhibited similar average molar masses between 10 000 and 15 000 g.mol⁻¹ and glass transition temperatures value of 73 and 88 °C for the polyimide based on PMDA/D-230 and BTDA/D-230, respectively. These polyimides started to degrade at temperatures over 300 °C under inert atmosphere. The synthesis of polyimides by reactive extrusion offers a fast and innovative way of producing aromatic-aliphatic polyimides, free of solvent compared to the more classical solvent based process. The key point is the control of the initial stoichiometry and the design of the screw profile to reach a complete conversion of the imidization reaction. From that control, this polyimide synthesis in one-step by reactive extrusion opens a new field to reach polyimides with high glass transition temperatures and high molar masses and thus enhanced mechanical properties in particular.

Acknowledgements

This research was supported by the French Ministry of Education and Research. We kindly thank Huntsman for providing some materials for this study.

References

1. Ma, P. C., Dai, C. T., Wang, H. Z., Li, Z. K., Liu, H. B., Li, W. M., Yang, C. L. A review on high temperature resistant polyimide films: Heterocyclic structures and nanocomposites. *Compos. Commun.*, **2019**, 16, 84-93
2. Tapaswi, P. K., Ha, C. S. Recent Trends on Transparent Colorless Polyimides with Balanced Thermal and Optical Properties: Design and Synthesis *Macromol. Chem. Phys.*, **2019**, 220 (3), special issue

3. Liaw, D. J., Wang, K. L., Huang, Y. C., Lee, K. R., Lai, J. Y., Ha, C. S. Advanced polyimide materials: Syntheses, physical properties and applications. *Prog. Polym. Sci.*, **2012**, 37, 907–974.
4. Finckenor, M. M. D. Multilayer Insulation Material Guidelines, National Aeronautics and Space Administration Marshall Space Flight Center • MSFC, Alabama 35812 **1999**
5. Heck, R., Qahtani, M. S., Yahaya, G. O., Tanis, I., Brown, D., Bahamdan, A. A., Ameen, A. W., Vaidya, M. M., Ballaguet, J-P. R., Alhajry, R. H., Espuche, E., Mercier, R. Block co-polyimide membranes for pure- and mixed- gas separation, *Sep. Purif. Technol.*, **2017**, 173, 183-192
6. Piroux, F., Espuche, E., Mercier, R., Pineri, M., Gebel G., Gas transport mechanism in sulfonated polyimides. Consequences on gas selectivity. *J. Membrane Sci.*, **2002**, 209 (1), 241-253
7. Genies, C., Mercier, R., Sillion, B., Cornet, N., Gebel, G., Pineri, M. Soluble sulfonated naphthalenic polyimides as materials for proton exchange membranes. *Polymer*, **2001**, 42, 359–373
8. Hickner, M. A., Ghassemi, H., Kim, Y. S., Einsla, B. R., McGrath, J. E. Alternative polymer systems for proton exchange membranes (PEMs). *Chem. Rev.*, **2004**, 104, 4587–4612.
9. Miyatake, K., Zhou, H., Watanabe, M. Proton conductive polyimide electrolytes containing fluorenyl groups: Synthesis, properties, and branching effect. *Macromolecules*, **2004**, 37, 4956–4960.
10. Asano, N., Aoki, M., Suzuki, S., Miyatake, K., Uchida, H., Watanabe, M. Aliphatic/aromatic polyimide Ionomers as a proton conductive membrane for fuel cell applications. *J. Am. Chem. Soc.*, **2006**, 128, 1762–1769.
11. Bogert, M. T., Renshaw, R. R. J. (4)-Amino-o-phthalic acid and some of its derivatives. *J. Am. Chem. Soc.*, **1908**, 30, 1135–1144.

12. Bower, G. M., Frost, L. W. Aromatic polyimides. *J. Polym. Sci. Part A General Papers*, **1963**, 1, 3135–3150.
13. Sroog, C. E., Endrey, A. L., Abramo, S. V., Berr, C. E., Edwards, W. M., Olivier, K. L. Aromatic polypyromellitimides from aromatic polyamic acids. *J. Polym. Sci. A*, **1965**, 3, 1373–1390.
14. Dine-Hart, R. A., Wright, W. W. J. Preparation and fabrication of aromatic polyimides. *Appl. Polym. Sci.*, **1967**, 11, 609–627.
15. Nosova, G. I., Koton, M. M., Laius, L. A., Sazanov, Y. N., Denisov, V. M., Nefedov, P. P., Lazareva, M. A. Direct synthesis of aromatic polyamic acids under the action of catalytic compositions *Polym. Sci. USSR*, **1985**, 27, 912–919
16. Volksen, W., Cotts, P. M. The synthesis of polyamic acids with controlled molecular weights In *Polyimides*, K. L. Mittal, Ed.; Springer US **1984**; 163–170.
17. Laius, L. A., Bessonov, M. I., Florinskii, F. S. Some characteristics of the kinetics of polyimide formation. *Polym. Sci. USSR*, **1971**, 13, 2257–2262.
18. Yu, H.-C., Jung, J.-W., Choi, J.-Y., Chung, C.-M. Kinetic Study of Low-Temperature Imidization of Poly(amic acid)s and Preparation of Colorless, Transparent Polyimide Films. *J. Polym. Sci. Part A. Polym. Chem.*, **2016**, 54, 1593–1602.
19. Endrey, A. L. Process for preparing polyimides by treating polyamide-acids with lower fatty monocarboxylic acid anhydrides. US3179630A **1962**.
20. Kailani, M. H., Sung, C. S. P. Chemical Imidization Study by Spectroscopic Techniques. 1. Model Amic Acids. *Macromolecules*, **1998**, 31, 5771–5778.
21. Silvi, N., Giammattei, M. H., Howson, P. E., Khouri, F. F. Method for preparing polyimide and polyimide prepared thereby. US7053168 B2 **2006**
22. E. I. DuPont de Nemour GB570858 (A) **1945**
23. Frosch, C. J. Linear polymer containing cyclic imide groups. US2421024 (A) **1947**
24. Edwards, W. M., Maxwell R. I. Polyimides of pyromellitic acid US2710853 (A) **1955**

25. Edwards, W. M., Maxwell R. I., Noonan S. E. Preparation of polypyromellitimides US2867609 (A) **1959**
26. Takekoshi, T., Kochanowski, J. E. Method for making polyetherimides US4011198A **1977**.
27. Schmidt, L. R., Lovgren, E. M., Meissner, P. G. Method for making polyetherimides US 4443592 **1984**.
28. Schmidt, L. R., Lovgren, E. M. Method for making polyetherimide. US 4443591A **1984**.
29. Avakian, R. W., Hu, L. Preparation of imide oligomers via concurrent reactive extrusion. WO2015048065A1 **2015**
30. Cao, Q., Crawford, D. E., Shi, C., James, S.L., Greener dye synthesis: continuous, solvent-free synthesis of commodity perylene diimides by twin-screw extrusion. *Angew. Chem. Int. Ed.* **2020**, 59, 4478 – 4483
31. Bounor-Legaré, V., Fenouillot, F., Cassagnau, P. " In situ synthesis of inorganic and/or organic phases in thermoplastic polymers by reactive extrusion" Wiley–VCH book “Reactive Extrusion”, edited by Dr. Günter Beyer and Dr.-Ing. Christian Hopmann **2016**
32. Cassagnau P. , Bounor-Legare V. ; Fenouillot F. Reactive processing of thermoplastic polymers: a review of the fundamental aspects. *International Polymer Processing*, **2007**, 22(3), 218-258
33. Brunel, R., Marestin, C., Martin, V., Mercier, R., Water borne polyimides via microwave assisted polymerization, *High Perf. Polym.*, **2010**, 22, 1, 82- 94
34. Harris, F. W., Synthesis of aromatic polyimides from dianhydrides and diamines. *Polyimides*, Ed. Wilson D., Stenzenberger, H.D., Hergenrother, P.M., Chapman and Hall, New York, 1990, Chapter 1, **1990**.
35. Ardashnikov, A. Y., Kardash, I. Y., Pravednikov, A. N. The Nature of the Equilibrium in the Reaction of Aromatic Anhydrides with Aromatics Amines and its Role in Synthesis of Polyimides, *Poly. Sci. U.S.S.R.* 13, 2092-2100, **1971**.

36. Anthamatten, M., Letts, S. A., Day, K., Cook, R. C., Gies, A. P., Hamilton, T. P., Nonidez, W. K. Solid-state amidization and imidization reactions in vapor-deposited poly(amic acid), *J. Polym. Sci. Part A, Polym. Chem.*, **2004**, 42, 5999–6010
37. Snyder, R. W., Thomson, B., Bartges, B., Czerniawski, D., Painter, P. C. FTIR studies of polyimides: thermal curing, *Macromolecules*, **1989**, 22, 4166–4172
38. Pyun, E., Mathisen, R. J., Sung, C. S. P. Kinetics and mechanisms of thermal imidization of a polyamic acid studied by ultraviolet-visible spectroscopy. *Macromolecules*, **1989**, 22, 1174–1183
39. Schab-Balcerzak, E., Janeczek, H., Kucharski, P. Influence of azobenzene units on imidization kinetic of novel poly(ester amic acid)s and polymers properties before and after cyclodehydration. *J. Appl. Polym. Sci.*, **2010**, 118, 2624–2633
40. Cho, D., Drzal, L. T. FT-IR studies on imidization and end-group reaction behaviors of a phenylethynyl terminated imide oligomer ICCM12 Conference Paris July **1999**, proceeding paper 684.
- 41 Culbertson, B. M., McGrath, J. E. *Advances in Polymer Synthesis*, Springer Science & Business Media, **1984**.
42. Seshadri, K. S., Antonoplos, P. A., Heilman, W. J. J. ^{13}C -NMR spectroscopy of polyamic acids and polyimides. *J. Polym. Sci. Polym. Chem. Ed.*, **1980**, 18, 2649–2662.
43. Grubb, T. L., Ulery, V. L., Smith, T. J., Tullos, G. L., Yagci, H., Mathias, L. J., Langsam, M. Highly soluble polyimides from sterically hindered diamines *Polymer*, **1999**, 40, 4279–4288
44. Sun, J., Wang, Y., Dou, S., Ruan, C., Hu, C. PEG derived hydrogel: A novel synthesis route under mild condition. *Mater. Lett.*, **2012**, 67, 215–218.
45. ACD/H+C NMR Predictor, version **2015**, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com.
46. Ando, S., Matsuura, T., Nishi, S. ^{13}C n.m.r, analysis of fluorinated polyimides and poly(amic acid)s. *Polymer*, **1991**, 33, 2934–2939.

47. Young, P. R., Escott, R. Characterisation of polyimides In Polyimides, D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds.; Springer Netherlands **1990**; pp. 129–157.
48. Koton, M. M., Meleshko, T. K., Kudryavtsev, V. V., Nechayev, P. P., Kamzolkina, Y. V., Bogorad, N. N. Investigation of the kinetics of chemical imidization. Polym. Sci. USSR, **1982**, 24, 791–800.
49. Chu, N.-J., Huang, J.-W. Reactivity of Poly(amic acid) Isomers in Thermal Imidization. Polym J, **1990**, 22, 725–732.
50. Belina, K., Polgàr, K., Birò, O., Varga, J. Production and investigation of polyimides 2. Investigation of thermal imidization of polyamide acids. Period. Polytech. Chem. Eng., **1978**, 22, 239.
51. Chang, J. H., Park, K. M., Lee, I. C. Thermal cyclodehydration of aromatic precursor polymers to polybenzoxazole and polyimide; their thermal and mechanical properties. Polym. Bull., **2000**, 44, 63–69.
52. Seo, Y., Lee, S. M., Kim, D. Y., Kim, K. U. Kinetic Study of the Imidization of a Poly(ester amic acid) by FT-Raman Spectroscopy. Macromolecules, **1997**, 30, 3747–3753.
53. Kim, Y. J., Glass, T. E., Lyle, G. D., McGrath, J. E. Kinetic and Mechanistic Investigations of the Formation of Polyimides under Homogeneous Conditions, Macromolecules **1993**, 26, 1344-1358
54. Yu, H. C., Jung, J. W., Choi, J. Y. , Chung, C. M., Kinetic Study of Low-Temperature Imidization of Poly(amic acid)s and Preparation of Colorless, Transparent Polyimide Films. J. Polym. Sci. Part A, Polym. Chem, **2016**, 54, 1593–1602
55. Tsapovetskii, M. I., Laius, L. A. Analysis of the thermal cyclization kinetics of solid-state polyamic acids. Polym. Sci. USSR, **1982**, 24, 1103–1108.
56. Jen, G., Huang, S. J., Sung, C. S. Characterization of the One Step Polyimide Synthesis, Connecticut Univ Storrs Inst of Materials Science, **1994**.
57. Krishnan, P. S. G., Veeramani, S., Vora, R. H., Chung, T. S., Uchimura, S. I., Sugitani, H. Molecular mass determination of polyamic acid ionic salt by size-exclusion chromatography. Journal of Chromatography A, **2002**, 977, 207–212

58. Konas, M., Moy, T. M., Rogers, M. E., Shultz, A. R., Ward, T. C., McGrath, J. E. Molecular weight characterization of soluble high performance polyimides. 1. Polymer-solvent-stationary phase interactions in size exclusion chromatography. *J. Polym. Sci. Part. B Polym. Phys.*, **1995**, 33, 1429-1439.
59. Konas, M., Moy, T. M., Rogers, M. E., Shultz, A. R., Ward, T. C., McGrath, J. E. Molecular weight characterization of soluble high performance polyimides. 2. Validity of universal SEC calibration and absolute molecular weight calculation, *J. Polym. Sci. Part. B Polym. Phys.*, **1995**, 33, 1441-1448.
60. Diaham, S., Locatelli, M.-L., Khazak, R. In *High Performance Polymers - Polyimides Based - From Chemistry to Applications*, M. Abadie, Ed.; InTech **2012**.
61. Eastmond, G. C., Paprotny, J. Polyimides with main-chain ethylene oxide units: synthesis and properties, *Polymer*, **2002**, 43, 3455-3468

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