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Chemically imidized semi-alicyclic polyimides: the effect of catalyst type and imidization temperature

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ABSTRACT

Polyimides are a group of polymers with excellent thermal and mechanical properties. However, generally, they exhibit brown coloration due to charge transfer interactions between diamine donor and dianhydride acceptor moieties. In this study, semi-alicyclic polyimides derived from cyclohexane tetracarboxylic dianhydride and 4,4′-oxydianiline were prepared using a two-step method, where the imidization step proceeded via a chemical route. The effects of the catalyst type (quinoline, triethylamine, and 1,4-diazabicyclo(2.2.2)octane (DABCO)) and reaction temperature (120, 140, and 160 °C) on the imidization process were evaluated using infrared spectroscopy and nuclear magnetic resonance spectroscopy. The prepared polyimides' thermal, mechanical, and optical properties were compared with those synthesized via standard thermal imidization. Polyimide films possessing favorable mechanical properties, thermal stability, and good optical transparency were prepared via a simple preparation route based on chemical imidization using the triethylamine catalyst at the reaction temperature of 160 °C, which was shown to be a promising way for the PI preparation on an industrial scale.

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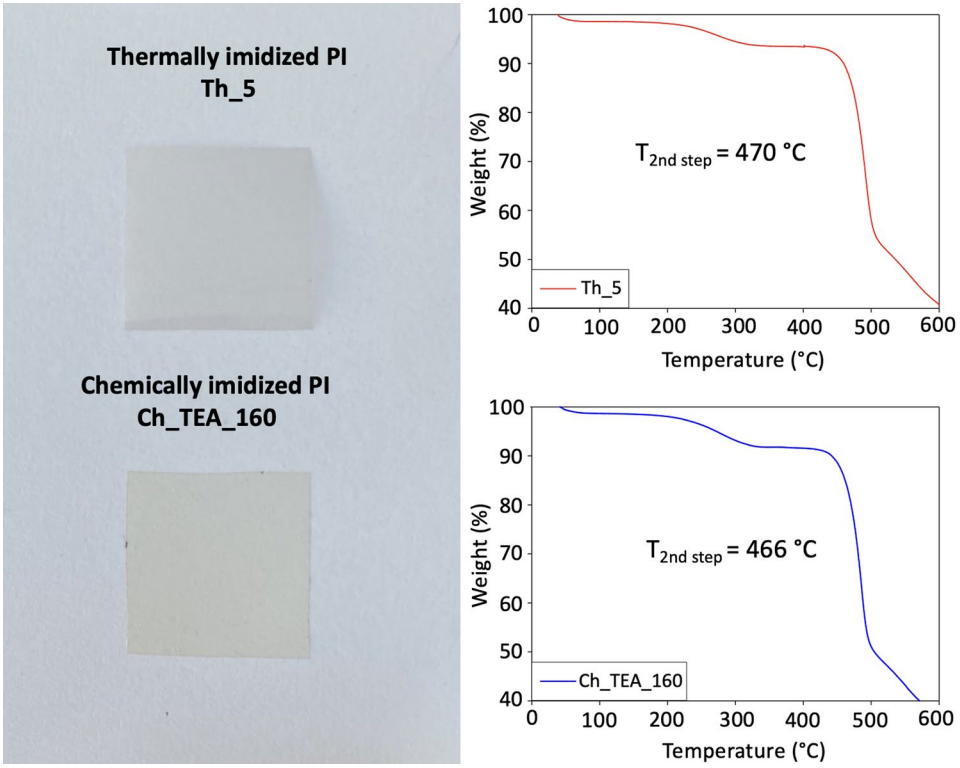
GRAPHICAL ABSTRACT



Introduction

Polyimides (PIs) form an important class of engineering polymers and are used in a wide range of applications. Due to their excellent properties, including thermo-oxidation stability, high resistance to radiation and solvents, and high mechanical strength, they are used as advanced materials in aerospace, microelectronics, biomedicine, sensors, optical devices, and many other applications [1–4]. The most widely used method for the preparation of PIs is a two-step method in which polyamic acid (PAA) is prepared from a diamine and a tetracarboxylic dianhydride in the first step [5]. The reaction usually takes place at ambient temperature in a polar aprotic solvent such as *N*,*N*-dimethylacetamide (DMAc [6, 7] or *N*,*N*-dimethylformamide [8] that can form strong hydrogen-bonded complexes with the carboxyl group shifting the equilibrium to the PAA side. Then, in the second step, PAA is converted to the corresponding PI via intramolecular cyclization (imidization) proceeding using a thermal or chemical method [9–11].

Among all the PI materials, the fully aromatic PIs are appreciated for the combination of extraordinary properties, namely high thermal stability, low dielectric constant, good mechanical properties, and chemical resistance. However, they suffer from yellowish nature, which limits their widespread applications in optoelectronics where colorlessness and transparency are the basic needs [12–14]. The coloration in aromatic PIs is attributed to the formation of the intra- and/or inter-molecular charge transfer (CT) complex between the alternating electron-accepting (dianhydride) and electron-donating (diamine) moieties [15–17]. In this regard, adopting the alicyclic moieties in the polymer structure has been found as an effective strategy for obtaining transparent and colorless PIs [18–21]. Unfortunately, the fully alicyclic PIs derived from alicyclic dianhydrides and diamines exhibit much lower thermal stability in comparison with the fully aromatic PIs [22–24]. On the contrary, the semi-alicyclic PIs synthesized from alicyclic dianhydrides and aromatic diamines have been shown to simultaneously maintain both transparency, high thermal stability, and mechanical

toughness [25–29]. For this reason, the PIs derived from 1,2,4,5-cyclohexanetetracarboxylic dianhydride (CHDA) and 4,4′-oxydianiline (ODA) were the subject of this study.

Currently, PIs are most often synthesized by a two-step method using thermal imidization, which produces materials with excellent thermal and mechanical properties [30, 31]. However, the thermal imidization process imparts several disadvantages. One of the shortcomings often lies in the impossibility of preparing a large amount of PI, with the exception of the roll-to-roll casting method providing continuous thin films [32]. In addition, completing the imidization process requires high temperatures (above 300 °C) and extremely low pressure, often also an inert atmosphere. Vacuum dryers capable of achieving these conditions are structurally complex, financially expensive, and spatially small. Moreover, wide conventional applications of PIs in electronic devices containing at least one or more thermally unstable organic compounds have been inferred so far. High temperatures during imidization may also result in the reduction of mechanical properties, peeling off, and cracking of PI products due to thermally induced internal stress [33, 34].

In recent years, attention has been turned to a simpler preparation route for PIs without the above-mentioned shortcomings. The solution has been offered by a two-step method using chemical imidization during which PAA is dehydrated and cyclized to PI already in the solution with the help of dehydrating agents or basic catalysts [35–38]. The dehydrating agent can be an aliphatic or aromatic acid such as acetic anhydride [39]. As the catalyst, an aliphatic tertiary amine (e.g., triethyl amine [40]), pyridine [41, 42]), or heterocyclic compounds (e.g., quinoline [41, 43], isoquinoline [41, 44]) can be utilized. Using the chemical route, dehydration and subsequent imidization of PAA can be performed at significantly lower temperatures (below 200 °C) compared to the thermal route [45]. The PI body must then be dried; however, this operation takes place at significantly lower temperatures and mild vacuum compared to thermal imidization conditions [38, 46]. The PI preparation process using chemical imidization also has the advantage of increasing the visible transmittance of the resulting PI film compared to the conventional two-step process based on thermal imidization [47, 48]. These benefits make the chemical imidization a very promising method for the preparation of PIs on an industrial scale, and further efforts to find more efficient catalysts are important for broadening industrial applications.

The aim of this work was to compare the influence of various catalysts (quinoline, triethylamine, and 1,4-diazabicyclo(2.2.2)octane (DABCO)) and reaction temperatures (120, 140, and 160 °C) during the chemical imidization of semi-alicyclic PIs on their properties. The PIs were derived from alicyclic dianhydride (CHDA) and aromatic diamine (ODA), which are the monomer representatives guaranteeing high visible-light transmission. The efficiency of chemical imidization was evaluated by Fourier transform infrared (FT-IR) analysis and the process of chemical imidization was also monitored by proton nuclear magnetic resonance (^{1}H NMR). Subsequently, the thermal, mechanical, and optical properties of the prepared PI films were studied.

Materials and methods

Materials

1,2,4,5-Cyclohexanetetracarboxylic dianhydride (CHDA) was purchased from Waco Pure Chemical Industries (Ósaka, Japan). 4,4′-Oxydianiline (ODA) and quinoline (QL) were purchased from Sigma-Aldrich (Darmstadt, Germany). *N*,*N*-Dimethylacetamide (DMAc) and triethylamine (TEA) were purchased from Penta (Prague, Czech Republic). 1,4-Diazabicyclo(2.2.2)octane (DABCO) was purchased from TCI (Tokyo, Japan). TEA was distilled before use; other chemicals were utilized as received.

Synthesis of polyimides

PI samples were synthesized using a two-step method. In the first step, performed in the case of all PI samples (Table 1), polyamic acid (PAA) was prepared from ODA and CHDA. 0.801 g (4 mmol) of ODA was dissolved in 7.3 ml of DMAc. After the dissolution, 0.897 g (4 mmol) of CHDA was added to the reaction mixture. The reaction mixture was then stirred for 24 h at ambient temperature in a dark place under a nitrogen atmosphere. In the second step, PAA was converted to PI via chemical or thermal imidization.

Table 1 List of the prepared PIs

Sample	Type of imidization	Catalyst	Amount of catalyst (g)	Imidization temperature (°C)	Vacuum (mbar)
Ch_QL_120	Chemical	QL	0.516	120	5
Ch_QL_140	Chemical	QL	0.516	140	5
Ch_QL_160	Chemical	QL	0.516	160	5
Ch_TEA_120	Chemical	TEA	0.405	120	5
Ch_TEA_140	Chemical	TEA	0.405	140	5
Ch_TEA_160	Chemical	TEA	0.405	160	5
Ch_DA_120	Chemical	DABCO	0.448	120	5
Ch_DA_140	Chemical	DABCO	0.448	140	5
Ch_DA_160	Chemical	DABCO	0.448	160	5
R_120	Catalyst-free	–	–	120	5
R_140	Catalyst-free	–	–	140	5
R_160	Catalyst-free	–	–	160	5
Th_5	Thermal	–	–	–	5
Th_0.007	Thermal	–	–	–	0.007

Chemical imidization

Synthesis of chemically imidized PIs was performed according to the following procedure. PAA was heated to 120, 140, and 160 °C, respectively. A specific catalyst (QL, TEA, and DABCO) in equimolar ratio to CHDA was subsequently added to the reaction mixture which was further stirred for 24 h at the respective temperature (120, 140, or 160 °C). In the case of QL and DABCO catalysts, the resulting PI was precipitated in water to remove the residues of the used catalyst. The precipitated PI was subsequently rinsed with water, dried in an oven for 2 h at 80 °C, and then subsequently dissolved in DMAc (20% dry weight). Since TEA has a low boiling point (approximately 90 °C), it was assumed that it was no longer present in the reaction mixture after the end of the imidization reaction; therefore, PIs prepared with this type of catalyst were only diluted to a dry matter content of 20 wt. % using DMAc without the precipitation in water. After that, the resulting PI solution was cast on a glass substrate using a blade applicator with a wet thickness of 500 µm. The film was dried in a vacuum oven (Fisher Scientific, Waltham, MA, USA) at the pressure of 5 mbar according to the following temperature program: 1) 120 °C for 1 h; 2) 130 °C for 1 h; 3) 150 °C for 1 h; 4) 170 °C for 2 h. Reference PI samples (R_120, R_140, and R_160) were synthesized in the absence of any catalyst. Their synthesis procedure otherwise proceeded in the same way as for the PIs prepared using the catalysts.

Thermal imidization

Synthesis of thermally imidized PIs proceeded as follows. The prepared PAA was cast on a glass substrate using a blade applicator with a wet thickness of 500 µm. The film was imidized at a high vacuum of 0.007 mbar in a furnace (VSK Pardubice s.r.o., Pardubice, Czech Republic) at the following temperature program: (1) heating to 150 °C at a heating rate of 5 °C min^{-1} followed by annealing for 1 h to remove the residual solvent; (2) heating to 250 °C at a heating rate of 5 °C min^{-1} and annealing for 1 h; and (3) heating to 300 °C at a heating rate of 5 °C min^{-1} followed by annealing for 2 h. After that, cracked PI films were obtained. The films were subsequently dissolved in DMAc (the concentration of the resulting PI solution was 20 wt%). The PI solution was cast on a glass substrate using a blade applicator with a wet thickness of 500 µm. The films were dried according to different procedures. Th_5 sample was dried in a vacuum oven at 5 mbar using the same temperature program set for the chemical imidization. Th_0.007 sample was dried at a high vacuum of 0.007 mbar in a furnace according to the same temperature program set for the thermal imidization. The schematic illustration of the preparation of PIs from ODA and CHDA via chemical and thermal routes is presented in Fig. 1.

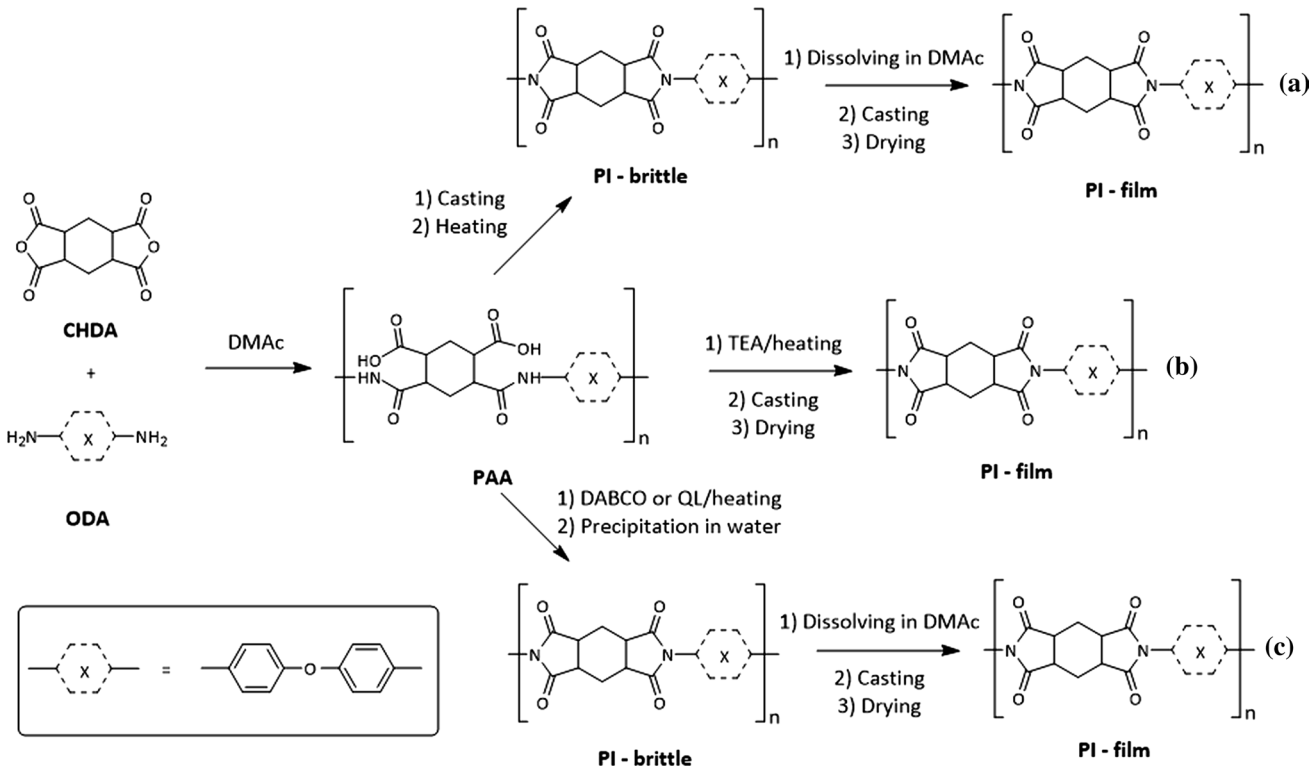


Figure 1 Synthesis and preparation of PIs: **a** thermal route; **b** chemical route using TEA; (**c**) chemical route using QL or DABCO.

Characterization

Infrared spectra were measured on Fourier transform infrared (FT-IR) spectrometer Bruker INVENIO X (Bruker, Billerica, Massachusetts, USA) by the attenuated total reflectance (ATR) method using a diamond crystal in the region of 4000–300 cm^{-1}. The imidization degree (ID) of dried PI films was calculated by a reported method [49]. In the calculation, the aromatic band at 1 500 cm^{-1} was selected as the internal standard and the band at 1720 cm^{-1} (C=O asymmetric stretching that is characteristic of the PI structure) or the band in the region of 1620–1600 cm^{-1} (C=O amide stretching that is characteristic for PAA) were selected for quantifying ID. ID was calculated using Eqs. (1), (2):

$$\mathrm{ID}\,(\%) = \frac{\left(\frac{S_{1720}}{S_{1500}}\right)_{\mathrm{Ch}}}{\left(\frac{S_{1720}}{S_{1500}}\right)_{\mathrm{Th\_0.007}}}.100 \tag{1}$$

$$\mathrm{ID}\,(\%) = \left(1 - \frac{\left(\frac{S_{1620-1600}}{S_{1500}}\right)_{\mathrm{Ch}}}{\left(\frac{S_{1620-1600}}{S_{1500}}\right)_{\mathrm{Th\_0.007}}}\right).100 \tag{2}$$

where S is the area of the absorption band at the respective wavenumber for the chemically (Ch) and thermally (Th_0.007) imidized PI sample which was taken as the completely imidized (reference) sample.

Ultraviolet–visible (UV–Vis) spectra were measured using a ColorQuest XE spectrometer (Hunterlab, Reston, Virginia, USA). Glass transition temperature (T_g) was measured using differential scanning calorimetry (DSC) on DCS 250 (TA Instruments, New Castle, Delaware, USA) under nitrogen gas flow with a heating rate of 20 °C min^{-1}. Thermogravimetric analysis (TGA) was carried out with a TGA Q500 (TA Instruments, New Castle, Delaware, USA) under nitrogen gas flow with a heating rate of 10 °C min^{-1}. Proton nuclear magnetic resonance (^{1}H NMR) spectra were measured at 25 °C using Magritek 60 MHz (Magritek, Aachen, Germany) and Bruker AdvancedTM 500 MHz (Bruker, Billerica, Massachusetts, USA) in dimethyl sulfoxide-d_6 as a solvent. The mechanical properties of samples were measured on a universal testing machine LabTest 6.50 (Labortech s.r.o., Prague, Czech Republic) according to ASTM D 1708.

Results and discussion

FT-IR analysis of imidization efficiency

Differences in the imidization degree of PIs prepared via a thermal and chemical route (differing in the catalyst type and imidization temperature) were monitored using FT-IR spectroscopy. The FT-IR analysis of the synthesized PIs was performed after completing the imidization and drying process. The bands, characteristic of the PI structure, at 1780 cm^{-1} (symmetric stretching vibration of C=O), 1720 cm^{-1} (asymmetric stretching vibration of C=O), and 1380 cm^{-1} (stretching vibration of C–N) [50, 51] were observed. Both thermally prepared PIs, differing in the subsequent drying procedure, showed almost identical infrared spectra, suggesting no significant impact of the drying conditions (defined especially by the vacuum intensity) on the imidization degree (Fig. 2).

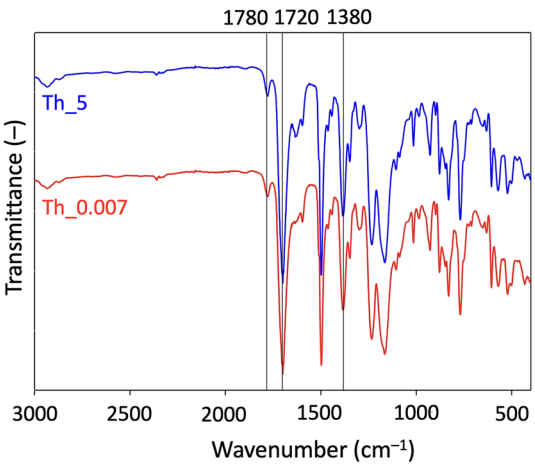


Figure 2 Infrared spectra of the thermally prepared PIs.

Infrared spectra of PIs prepared by the chemical route are presented in Fig. 3. For all series of PIs differing in the catalyst type, the intensity of the characteristic bands increased with the growing imidization temperature (this effect can be most clearly seen for the band of C=O asymmetric stretching at 1720 cm^{-1}), which indicates the increased PAA conversion into PI via intramolecular cyclization. The most significant influence of the temperature on the imidization degree can be observed for reference PIs prepared without any catalyst (Fig. 3d). It is evident from the signal intensities that the degrees of intramolecular cyclization performed without a catalyst at 120 and 140 °C were significantly lower in comparison with PIs

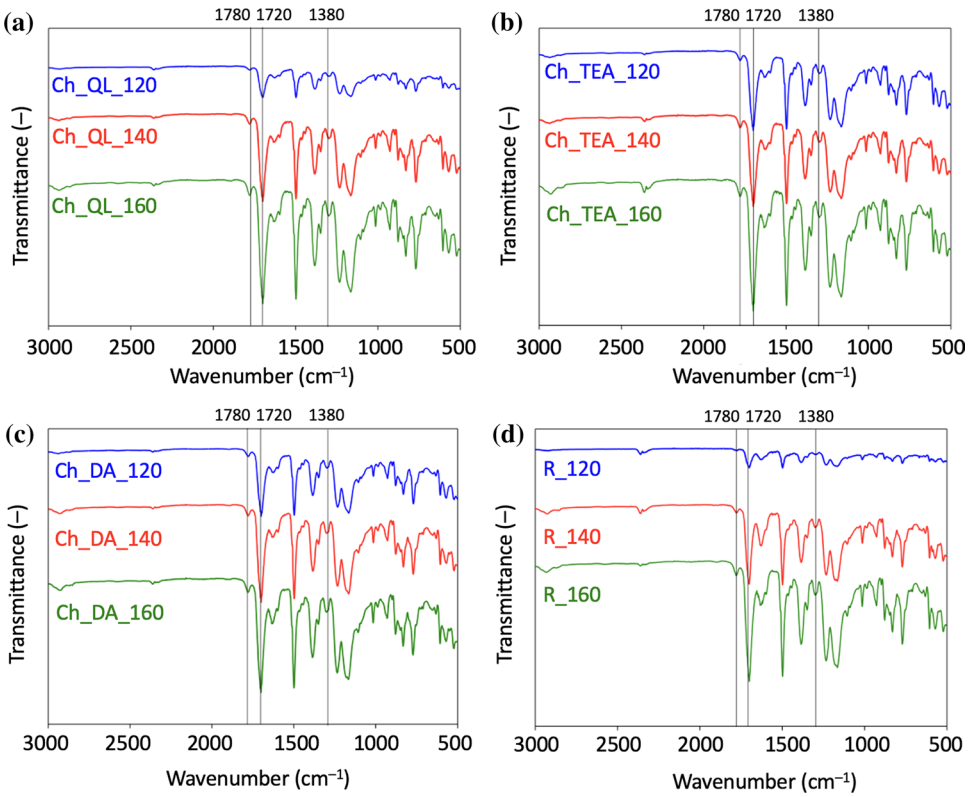


Figure 3 Comparison of the chemically imidized PIs differing in the imidization temperature and catalyst type: **a** QL; **b** TEA; **c** DABCO; **d** catalyst-free.

prepared at the same temperatures in the presence of various catalysts. Using the imidization temperature of 160 °C, the intensities of the observed signals were almost comparable for all the chemically imidized PIs prepared regardless of the catalyst type and presence, which suggests a similar percentage of imidization.

The imidization degree was also monitored according to the intensity of C=O amide stretching observed in the region of 1620–1600 cm^{-1} [51] (Fig. 4), which corresponds to the presence of unreacted amic acid in the PI sample and indicates incomplete intramolecular cyclization. A high percentage of imidization is a condition for the preparation of cohesive and mechanically stable films. When comparing the intensity of this band in the spectrum of PAA with the intensity in the spectra of PIs imidized at 160 °C (in the absence/presence of different catalysts) and the PI sample imidized thermally, all the chemically and reference PIs comprised a significant percentage of amic acid. The conversion of the imidization reaction increased in the order: 1. chemical imidization in the absence of a catalyst, 2. chemical imidization using DABCO or TEA, 3. chemical imidization using QL, and 4. thermal imidization.

To quantify the effect of various catalysts and reaction temperatures on the chemical imidization process, the imidization degrees for individual PI samples were calculated using the characteristic bands of PI and PAA structures at 1720 cm^{-1} and 1620–1600 cm^{-1}, respectively (Table 2). It can be said that the results based on the characteristic band of the PI structure are consistent with the statements made above, but still, they can only be considered as a rough estimate of the achieved level of intramolecular cyclization. Comparing the data, the calculation based on the characteristic band of the PAA structure does not seem reliable enough because of interference with the absorption band of the hydroxyl group.

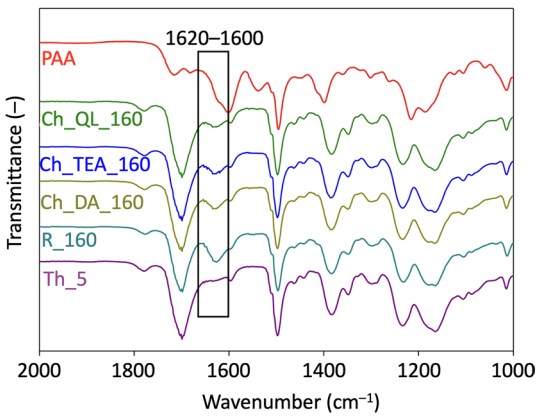


Figure 4 Comparison of the absorption band of amide stretching at 1620–1600 cm^{-1} in the infrared spectra of PAA with chemically, thermally, and catalyst-free imidized PI representatives.

^{1}H NMR analysis of chemical imidization reaction and prepared PIs

The course of the chemical imidization reaction was monitored by ^{1}H NMR (Fig. 5). The polymerizing samples were evaluated over time (after 1, 2, 3, 4, 5, and 24 h) by measuring the intensity of the amide (−CONH−) signal at 9.8 ppm which decreased as the reaction was proceeding (Fig. 6). The integral intensity of the amide signal was related to the signal of the aromatic ring at 6.5–8.5 ppm which remained constant during the reaction. It was demonstrated that the conversion of PAA to PI was significantly temperature-dependent for the series of PIs synthesized using the QL catalyst and for the series prepared in the absence of a catalyst. Specifically, the imidization performed at 160 °C using QL was almost completed after 2 h, whereas at 120 °C in the presence of the same catalyst the cyclization of PAA was not finished even after 20 h (Fig. 5a). TEA (Fig. 5b) and DABCO (Fig. 5c) were found to be highly effective catalysts performing similarly at all tested imidization temperatures. It was further verified that imidization could proceed to

Table 2 Comparison of the imidization degree (ID) calculated by FT-IR spectroscopy using: (**a**) the band at 1720 cm^{-1} (C=O asymmetric stretching) that is characteristic of the PI structure; (**b**) the band in the region of 1620–1600 cm^{-1} (C=O amide stretching) that is characteristic for PAA

Sample	ID (%)	
	(a)	(b)
Ch_QL_120	85	77
Ch_QL_140	92	85
Ch_QL_160	99	86
Ch_TEA_120	89	72
Ch_TEA_140	92	73
Ch_TEA_160	95	76
Ch_DA_120	91	73
Ch_DA_140	94	74
Ch_DA_160	97	78
R_120	71	33
R_140	87	51
R_160	94	77
Th_5	~100	~100
Th_0.007	100	100

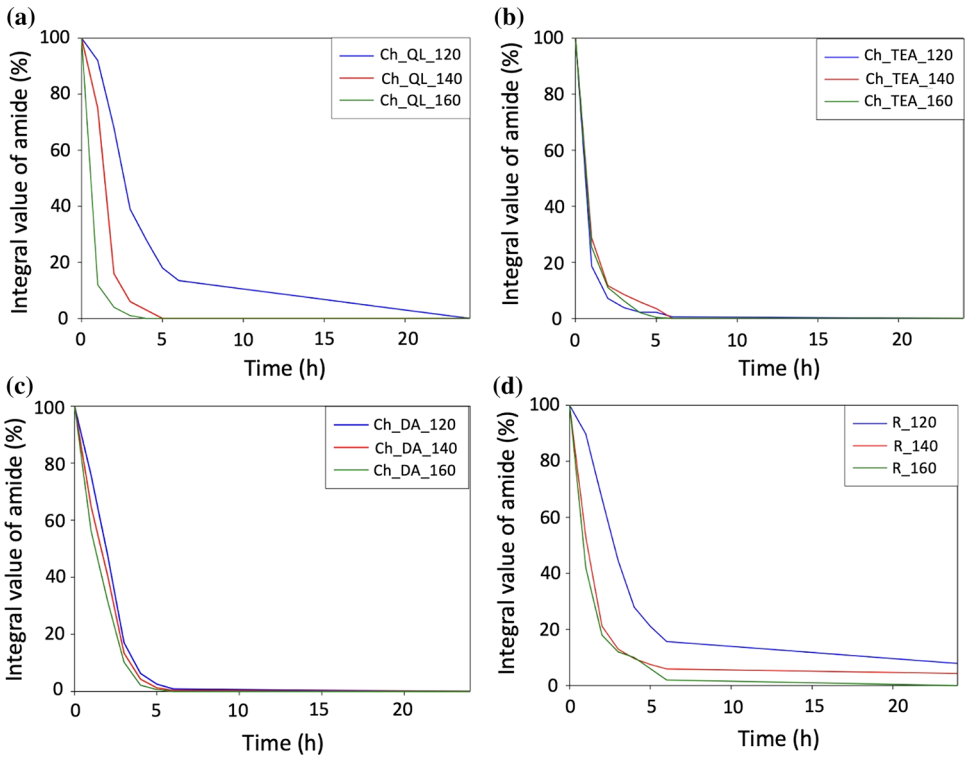


Figure 5 Graphs showing the integral value of the amide signal as a function of reaction time for the chemically imidized PIs prepared using different catalyst types: **a** QL; **b** TEA; **c** DABCO and **d** catalyst-free.

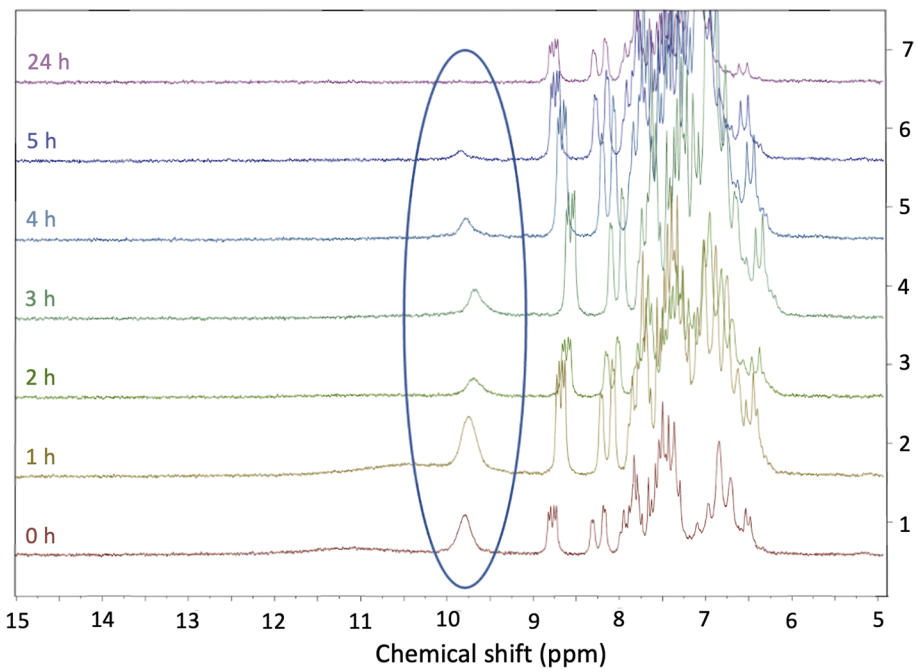


Figure 6 ^{1}H NMR spectra monitoring the conversion of PAA to PI by chemical imidization using QL at 120 °C as a function of time.

some extent without the help of any catalyst (Fig. 5d). However, in this case, the reaction temperatures of 120 and 140 °C were not sufficient to fully convert PAA to PI even during 24 h. Among the studied catalysts, TEA was shown to behave the most efficiently considering reaction temperatures of 120 and 140 °C, whereas QL was found to be the most effective catalyst at 160 °C, which also correlates with FT-IR results (Fig. 3).

The prepared PIs were investigated by ^{1}H NMR. The catalyst residues were evidenced in all the samples prepared by the chemical route using QL and DABCO, which is demonstrated in Fig. 7 showing the presence of QL in the Ch_QL_160 PI sample. In the case of the PIs synthesized chemically using TEA, no catalyst residues were detected, which indicates complete evaporation of TEA (having a boiling point of 89.3 °C) during PI preparation. Further, a significant amount of residual DMAc (exhibiting the signal at 2.94 and 2.78 ppm) was detected in all the mild-vacuum-dried samples i.e., in the chemically imidized PIs and the thermally imidized sample Th_5. The evidence of an increased DMAc content in PI representatives Ch_TE_160 and Th_5 in contrast to the high-vacuum-dried PI sample Th_0.007 is illustrated in Fig. 8.

Mechanical properties of PIs

Tensile strength (σ_m) and elongation at break (ε_b) were evaluated only for the PI samples found in the state of undivided (i.e., uncracked) films (Table 3). As for the integrity of the films, cracked and not cohesive PI films were prepared via the imidization without any catalyst regardless of the selected imidization temperature (in the case of all reference PIs), and by means of the chemical imidization at the lowest temperature (120 °C) with the help of any of the tested catalysts. In addition, a temperature of 140 °C during the chemical imidization using the TEA catalyst was also not sufficient for the formation of undivided films. Thus, it was found that the chemical imidization providing cohesive films needs to be performed using some of the tested catalysts

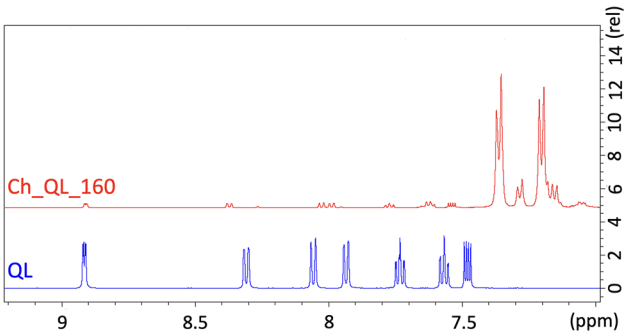


Figure 7 Comparison of ^{1}H NMR spectra of the QL catalyst and the Ch_QL_160 polymer sample.

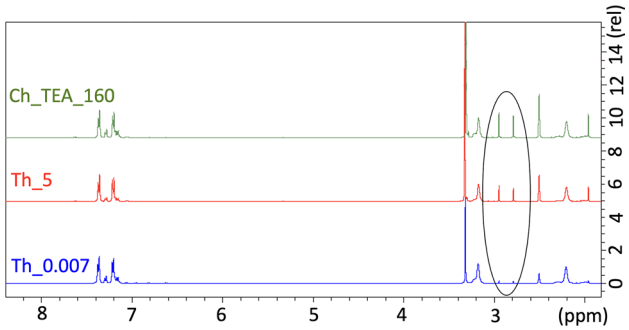


Figure 8 Comparison of ^{1}H NMR spectra of PI representatives differing in the intensity of DMAc signal at 2.94 and 2.78 ppm.

and simultaneously at the reaction temperature of 160 °C.

Tensile measurements revealed that similar tensile strength values were obtained for all the measurable PI samples except for the sample Ch_DA_140, indicating its poor cohesion. On the contrary, significant differences were found in the case of ductility. As expected, favorable ductility was found for thermally imidized PIs, comprising no catalyst impurities. Surprisingly, however, an approximately double value of elongation at break (with respect to the thermally imidized PI samples) was obtained for the sample Ch_TEA_160 (PI imidized chemically at 160 °C using the TEA catalyst). This phenomenon might be attributed to polymer plasticization by DMAc interacting with

Table 3 Mechanical properties of the prepared PIs

Sample	Film integrity	Mechanical properties	
		σ_m (MPa)	ε_b (%)
Ch_QL_120	No	–[a]	–[a]
Ch_QL_140	Yes	126 ± 5	8.1 ± 0.5
Ch_QL_160	Yes	128 ± 9	8.2 ± 1.5
Ch_TEA_120	No	–[a]	–[a]
Ch_TEA_140	No	–[a]	–[a]
Ch_TEA_160	Yes	119 ± 3	98.6 ± 13.1
Ch_DA_120	No	–[a]	–[a]
Ch_DA_140	Yes	52 ± 18	2.6 ± 0.7
Ch_DA_160	Yes	121 ± 6	22.9 ± 14
R_120	No	–[a]	–[a]
R_140	No	–[a]	–[a]
R_160	No	–[a]	–[a]
Th_5	Yes	134 ± 4	55.9 ± 14.2
Th_0.007	Yes	131 ± 15	46.9 ± 5.5

[a]Not measured because of film discontinuity

carboxyl groups. In contrast to the thermally imidized samples, more carboxyl groups were present in the polymer of the Ch_TEA_160 sample due to incomplete PAA cyclization (see Fig. 4).

Thermal properties

The T_g and thermal stability of the prepared PIs were measured by DSC and TGA under an inert atmosphere, respectively (Table 4). As for T_g results, it was shown that the temperature of chemical imidization did not affect the T_g significantly in contrast to the catalyst type. The highest T_g value (326 °C), indicating the highest percentage of PAA cyclization, was detected for the thermally imidized sample Th_0.007, which meets expectations and is consistent with previously mentioned results presented in Fig. 4. Surprisingly, high T_g values in the range of 313–323 °C were detected for the series of catalyst-free imidized reference samples, which could be explained by the absence of catalyst residues in the polymer structure. For these samples, the effect of increasing reaction temperature on T_g enhancement can be observed. In the case of the chemically synthesized PIs using any of the tested catalysts, decreased T_g values, being almost independent of the imidization temperature, can be assigned to DMAc plasticization due to polar catalyst residues and incomplete PAA cyclization resulting in carboxyl functionalities in PI structure.

Concerning the results of thermal stability, TGA demonstrated that except for the high-vacuum-dried sample (Th_0.007), all the prepared PIs showed a two-step thermal degradation (Figs. 9 and 10). In the first step occurring in the temperature range of approximately 165–230 °C, entrapped DMAc was released from the polymer, whereas the real polymer degradation occurred in the second step. (In all TGA curves, a slight weight loss can already be observed below 100 °C, which was probably caused by relatively high absorption of moisture into prepared PIs that had not been dried to constant weight before the measurement.) Comparing the values of weight loss during the first step which may also include released water as a by-product of additional imidization, it was found that an increased weight loss was detected in the samples prepared by the catalyst-free imidization at 120 and 140 °C (weight loss above 17 and 15 wt%, respectively). Therefore, the extent of weight loss in the first degradation step may also indicate the number of carboxyl functionalities that are inversely proportional to the degree of PAA cyclization. As for the real degradation of PI chains occurring in the second step, a significant influence of the imidization temperature on the onset of thermal degradation was proven only in the case of the series of chemically imidized PIs based on QL and DABCO catalysts. In addition, QL and DABCO catalysts were found to provide PIs exhibiting decreased thermal stability, which suggests a promoting effect of catalyst ingredients on thermo-chemical polymer decomposition. The series of chemically imidized PI samples using the TEA catalyst and the catalyst-free

Table 4 Thermal characteristics of the prepared PIs in terms of the glass transition temperature, the weight loss during the first degradation step, and the temperature representing the onset of the second degradation step

Sample	T_g (°C)	Weight loss at the first step (wt%)	$T_{second\ step}$ (°C)
Ch_QL_120	293	8.4	428
Ch_QL_140	304	9.2	432
Ch_QL_160	306	9.1	443
Ch_TEA_120	303	10.4	472
Ch_TEA_140	305	8.2	467
Ch_TEA_160	303	6.3	466
Ch_DA_120	317	10.4	426
Ch_DA_140	312	8.2	432
Ch_DA_160	319	6.9	453
R_120	313	17.8	482
R_140	318	15.6	480
R_160	323	9.0	479
Th_5	302	6.6	470
Th_0.007	326	0	471

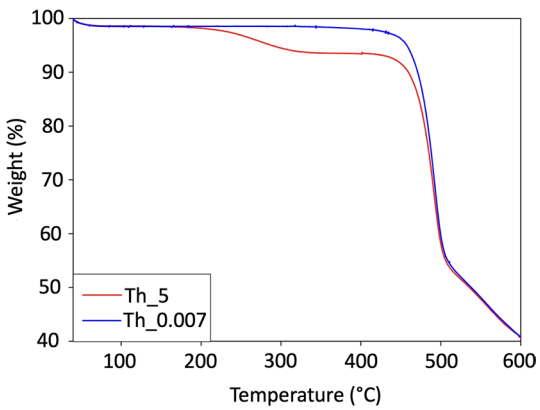


Figure 9 Comparison of TGA curves of the thermally prepared PIs.

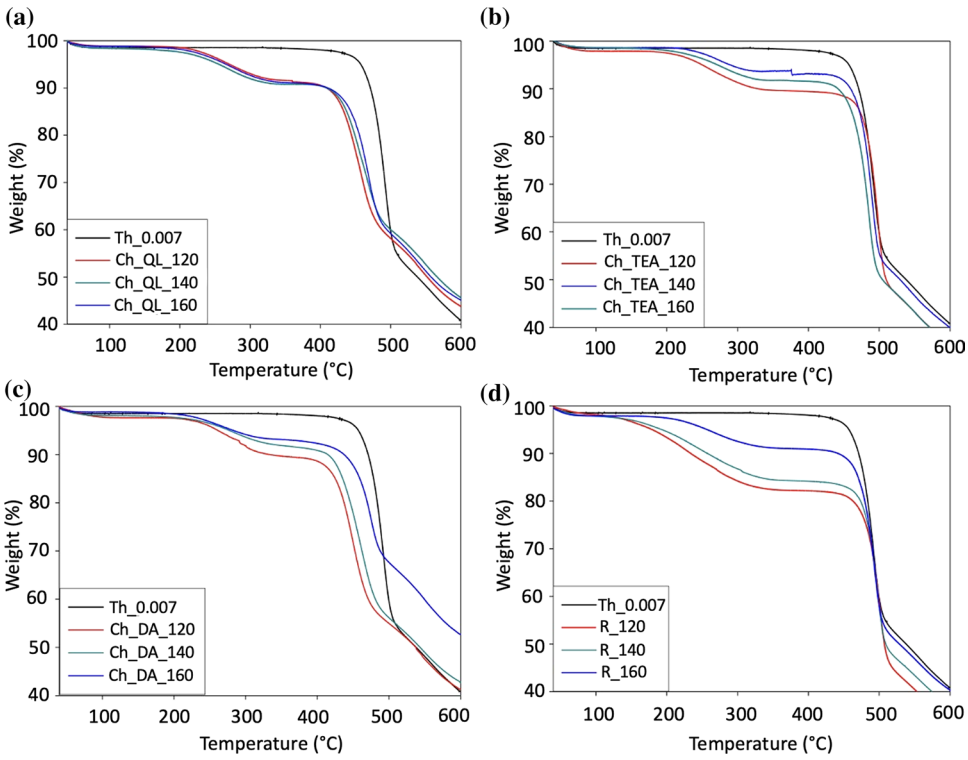


Figure 10 Comparison of TGA curves of the thermally (high-vacuum-dried) and chemically imidized PIs differing in the imidization temperature and catalyst type: **a** QL; **b** TEA; **c** DABCO; **d** without catalyst.

imidized reference PIs exhibited similar thermal degradation behavior to the thermally imidized PIs, which can be attributed to the absence of any catalysts in the resulting PI structure.

Optical properties

Figure 11 shows the optical photographs of all chemically imidized PIs that were prepared in the state of undivided films (film thickness of 40–50 μm). In comparison with the thermally imidized sample Th_0.007 that was clear to the eye, the chemically imidized PIs showed deterioration of optical transparency, and especially the PIs prepared using DABCO catalyst had a strongly yellowish nature. The difference in optical transparency between the cohesive PI films (~ 45 μm) was also monitored by UV–vis spectroscopy (Fig. 12). In addition, transmittance values at 400 and 700 nm (T_{400} and T_{700}, respectively) and the cut-off wavelength (λ_{cut}, λ at $T \sim 1\%$) were evaluated (Table 5). Among the chemically imidized PIs, the highest transmittance values were obtained for the sample Ch_TEA_160, which is probably related to the absence of catalyst impurities. Concerning the results of λ_{cut}, all the chemically imidized cohesive PI films exhibited enhanced λ_{cut} in comparison with the thermally imidized samples. The lowest value of λ_{cut} was obtained again for the

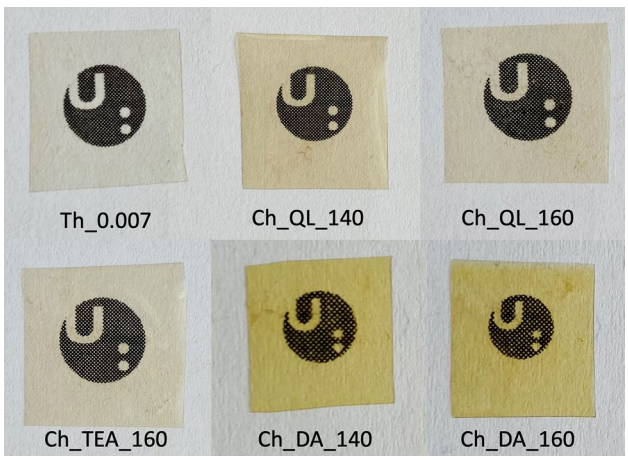


Figure 11 Photographs of cohesive PI films (40–50 μm).

Ch_TEA_160 sample whose optical properties were found the best among the chemically prepared cohesive PIs.

Comparison with PIs reported in the literature

PI films with excellent thermal stability ($T_g > 300$ °C), suitable mechanical properties, and high optical transparency ($T > 85\%$ in the visible-light region) are in demand, especially in optoelectronic applications. The

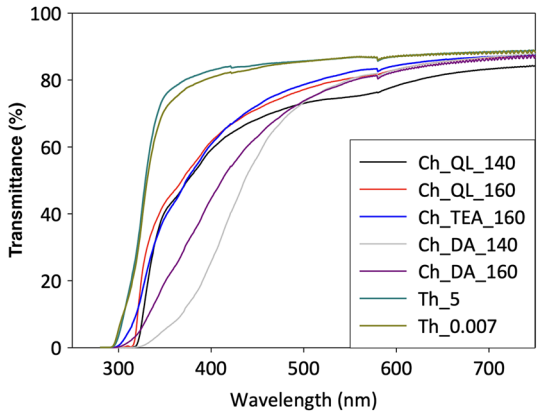


Figure 12 UV–vis spectra of cohesive PI films (~45 µm).

Table 5 Optical properties of the prepared PI films (~45 µm)

Sample	Optical properties		
	λ_{cut} (nm)	T_{400} (%)	T_{700} (%)
Ch_QL_120	–[a]	–[a]	–[a]
Ch_QL_140	320	58	83
Ch_QL_160	316	60	87
Ch_TEA_120	–[a]	–[a]	–[a]
Ch_TEA_140	–[a]	–[a]	–[a]
Ch_TEA_160	302	63	87
Ch_DA_120	–[a]	–[a]	–[a]
Ch_DA_140	329	26	87
Ch_DA_160	307	45	86
R_120	–[a]	–[a]	–[a]
R_140	–[a]	–[a]	–[a]
R_160	–[a]	–[a]	–[a]
Th_5	296	83	88
Th_0.007	295	82	88

[a]Not measured because of film discontinuity

latest research progress in this field (covering fluorinated, sulfur-containing, alicyclic, semi-alicyclic, and hybrid PIs) has been reviewed in several articles [52–54]. Among the papers on semi-alicyclic PI materials, those dealing with the chemically imidized PIs derived from CHDA and ODA were the center of our attention. The properties of the sample Ch_TEA_160, showing the best properties among the chemically imidized PIs prepared in this study, and the PI materials reported in the literature [55, 56] are compared in Table 6.

In terms of mechanical properties, the sample Ch_TEA_160 showed a similar tensile strength value as the reference PIs; however, it exhibited a distinctly higher ductility, which can be considered a beneficial feature. In the case of thermal stability, Ch_TEA_160 did not deviate significantly from the PIs reported in the literature. However, worse results were found for Ch_TEA_160 in terms of optical properties. Compared to both reference PIs, Ch_TEA_160 achieved a comparable λ_{cut} value, but significantly lower optical transmittance (T_{400}). This fact can be partly attributed to the approximately double thickness of the sample; however, the main contribution of the decrease in optical transparency is probably due to the partial oxidation of amine groups during imidization, being performed under an air atmosphere (in contrast to a nitrogen atmosphere applied in the case of both PIs reported in the literature). On the other hand, the procedure used in this research did not use toxic and corrosive chemicals (such as pyridine and acetic anhydride in reference [56]) and did not require additional processing steps including precipitation and subsequent dissolution of PI (being a part of the preparation route of both reference PIs). These benefits make this procedure a promising method for the preparation of PIs on an industrial scale.

Conclusions

In this work, the effects of catalyst type (quinoline, triethylamine, and 1,4-diazabicyclo(2.2.2)octane (DABCO)) and reaction temperature (120, 140, and

Table 6 Comparison of properties of the sample Ch_TEA_160 with relevant chemically imidized PIs (derived from CHDA and ODA) reported in the literature [55, 56]

Property	Ch_TEA_160	References	
		[55]	[56]
Catalyst	TEA	Isoquinoline	Acetic anhydride/pyridine
σ_m (MPa)	119	117	145
ε_b (%)	98.6	7.8	65.0
T_g (°C)	303	333	302
T_5 (N_2) (°C)	466[a]	442	–[b]
λ_{cut} (nm)	302	293	306
T_{400} (%)	63	84	93
Film thickness[c] (µm)	~45	~25	~20

[a]Start of polymer degradation after residual solvent evaporation

[b]Not mentioned in the reference

[c]Film thickness for optical transparency measurements

160 °C) on the process of chemical imidization and the resulting properties of polyimides, synthesized from cyclohexane tetracarboxylic dianhydride and 4,4′-oxydianiline, were studied with the aim to develop thermally and mechanically resistant materials transparent to visible light. It was found that cohesive polyimide films were prepared in the case of quinoline at 140 and 160 °C, while the imidization temperature of 160 °C was needed in the case of triethylamine and DABCO. Among the tested catalysts and reaction temperatures, polyimides synthesized at 160 °C using triethylamine showed excellent ductility. This phenomenon was assigned to incomplete imidization, where a sufficient degree of polyamic acid cyclization was achieved, providing film cohesion, while some carboxyl groups remained in polyimide chains, which enabled polymer plasticization by reaction solvent. The results also revealed that polyimides synthesized using quinoline and DABCO exhibited decreased thermal stability, most probably due to catalyst residues promoting polymer decomposition. The catalyst impurities were also responsible for the deterioration of optical transparency. On the contrary, triethylamine (with a low boiling point) evaporated completely during polyimide preparation and provided chemically imidized materials of the highest thermal stability and transparency to visible light. Another benefit of using the triethylamine catalyst was the absence of additional processing steps including precipitation and subsequent dissolution of the polyimide product that could be immediately cast into desired shapes and forms. It can be concluded that the chemical imidization performed at 160 °C using triethylamine as the catalyst provided polyimides having favorable mechanical properties, excellent ductility, high thermal stability, and good optical transparency, which makes this procedure a promising method for the preparation of PIs on an industrial scale.

Supplementary Information

The manuscript contains no supplementary materials.

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All authors contributed equally.

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Data availability

Data will be made available on request.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval There are no ethical issues involved in this study.

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