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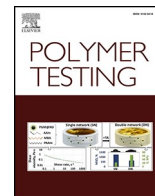
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Insights on the polymerization kinetics of non-isocyanate polyurethanes (NIPU) using *in situ* NMR spectroscopy

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ABSTRACT

An *in situ* characterization method using liquid Nuclear Magnetic Resonance (NMR) spectroscopy has been developed to aid the preparation of highly reactive non-isocyanate polyurethanes (NIPUs) from cyclic carbonate aminolysis. Using this methodology, the aminolysis kinetics and the final polymer structure of a model NIPU obtained by reaction of a 5-membered bis-cyclic carbonate (5CC) and 1,4-diaminobutane have been fully investigated, as a function of the type and concentration of the aminolysis catalyst, and the reaction temperature. Several catalysts already reported in NIPUs syntheses, including 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), have been compared. The kinetics of the 5CC hydrolysis side reaction was also studied. With an activation energy of 29.7 kJ mol⁻¹, TBD was clearly the most efficient catalyst used, allowing 5CC conversion ratio of up to 100 % using a concentration of 0.35 eq_{5CC}. However, under these experiment conditions, TBD concentration also showed to have a non-negligible influence on the hydrolysis rate, representing between 6 and 14 % of the initial 5CC concentrations, at 353 K. Neither the catalyst or the temperature seemed to affect the polymer structure, with secondary hydroxyl-containing isomer proportions of (70 ± 6) %. Finally, this *in situ* NMR method is paving the way for rapid screening of innovative catalysts for sustainable NIPU synthesis.

Abbreviations

5CC	5-membered cyclic carbonate	NMR	Nuclear magnetic resonance
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene	TBD	1,5,7-triazabicyclo[4.4.0]dec-5-ene
Ea	Activation energy	TU	1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea
k _{Am}	Aminolysis rate constant	TU ⁻	TU anionic form
NIPU	Non-isocyanate polyurethane		

1. Introduction

Polyurethanes (PUs) have been at the forefront of synthetic polymer innovation for over 80 years, occupying a prominent position in the

market [1,2], serving as assembling elements in transportation and construction, thermal/acoustic insulators, and core components in comfort items such as pillows and mattresses, among others [3–5]. Nevertheless, PUs are under regulatory scrutiny, particularly under the REACH regulation, for their negative impact on health and environment. In fact, they are obtained from the reaction between polyols and highly reactive aromatic diisocyanates, which are hazardous substances produced industrially from toxic phosgene. In this context, the substitution of conventional PUs by polyhydroxyurethanes synthesized from the aminolysis of poly(cyclocarbonates) obtained by CO₂ sequestration, is of great interest [6–8]. Despite their sustainability advantages, these molecules exhibit lower reactivity than isocyanates, resulting in longer curing times for Non-Isocyanate Polyurethane (NIPU) formulations, which are currently incompatible with the expected production rates of PUs in industrial applications. Moreover, due to the formation of a large number of hydrogen bonds during crosslinking of NIPUs, final

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conversions of cyclic carbonates (CC) generally do not exceed 80–85 % [9,10]. On the other hand, crosslinking NIPUs at temperatures higher than 373 K considerably increases the production of by-products such as ureas, amides, oxazolidinones or imidazolidinones, due to numerous side reactions [11].

In this context, the development of highly reactive NIPU systems is clearly one of the major challenges currently facing the PU industry. Numerous research teams have studied the reactivity of NIPU formulations, focusing on the chemical structure of both CC and amines [12–15] and the presence of specific substituents near these reactive groups [16, 17]. The influence of various organic bases, alkali metal salts, organometallic catalysts and Brønsted acids, on the aminolysis kinetics has also been studied [4,5,18]. A recent review by Kim et al. has highlighted the catalytic performance of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) in polymer synthesis [19], due to its unique chemical ability to act as both a proton donor and acceptor [20–22]. TBD was clearly the most studied catalyst in published papers dealing with NIPU catalysis (>160 articles on TBD catalysis). TBD exhibits superior efficiency in the aminolysis reaction due to its dual catalytic sites, which enhance both the nucleophilicity of the amine and the electrophilicity of the CC carbonyl [23, 24]. In addition, its aromatic structure facilitates the reaction by reducing the distance between the CC and the amine during nucleophilic attack. However, the catalytic performance of TBD may be affected under humid conditions, due to its water sensitivity [25]. For aqueous NIPU formulations, potassium hydroxide [26] or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [27] have been preferred for catalysing aminolysis. On the other hand, some thiourea-based catalysts, such as 1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea (TU) [9,24] and its anionic form (TU^-) [28], have recently been proposed, with potentially better results than TBD at lower catalyst concentrations. The advantage of these thiourea-based catalysts lies in the high acidity generated by the bis(trifluoromethyl)phenyl rings, which leads to a strong electron-withdrawing behaviour on the amine part of the thiourea, and thus to an efficient electrophilic activation of the CC carbonyl, promoting the nucleophilic attack of the primary amine.

Despite the quality of all these studies, it remains difficult to compare the efficiency of all catalysts, mainly due to the widespread use of TBD and the lack of comparative studies. Moreover, in such studies, the aminolysis kinetics were mainly measured either by direct physical methods, such as gelation time determination using plate-plate rheology, but without indication on the chemical structure of the final NIPU [29]; or by indirect chemical methods, such as Nuclear Magnetic Resonance (NMR) spectroscopy analyses of synthesized NIPU samples, with limitations on the number of samples characterized [30]. Therefore, the development of highly reactive NIPU formulations and the simultaneous study of the evolution of the polymer chemical structure, require a robust *in situ* characterization method. *In situ* NMR spectroscopy is a powerful tool that has been applied to a wide variety of polymer systems [31,32], especially for monitoring crosslinking reactions in polymers [33–35].

In the present work, an innovative methodology based on *in situ* liquid NMR spectroscopy has been developed to rapidly identify the most favorable conditions for the production of NIPU materials. Based on a previously reported bis-functional 5-membered cyclic carbonate (5CC) [30], several NMR methods, including 1H , ^{13}C and two-dimensional (2D) NMR, were used to study different catalysts including TBD, DBU and TU, as well as the influence of their concentration and the reaction temperature on the kinetic of polymerization. This approach was then used to calculate the activation energy of the different catalysts used to obtain linear NIPU systems. The stereochemistry of the final NIPU, depending on the experimental conditions is also discussed.

2. Experimental

2.1. Materials

Bisphenol A diglycidyl ether (DGEBA), TBD (98 %), DBU (98 %), butylamine (98 %), bis(trifluoromethyl)phenyl isothiocyanate (98 %), anhydrous and inhibitor-free tetrahydrofuran (THF, $\geq 99.9\%$), hexane ($\geq 95\%$), anhydrous N-methyl-2-pyrrolidone (NMP, 99.5 %), potassium methoxide and deuterated dimethyl sulfoxide (DMSO- d_6) and chloroform ($CDCl_3$) were provided by Sigma-Aldrich (France), tetrabutylammonium bromide (TBAB, 98 %) by Sodipro (France) and 1,4-diaminobutane (99 %) by Alfa Aesar (France). All chemicals were used as received.

2.2. Synthesis of 5-membered bis-cyclic carbonate of bisphenol A ether (5CC-EBA)

DGEBA (23 g, 67.56 mmol), TBAB (435 mg, 1.35 mmol) and 50 mL of NMP were placed in a 600 mL Parr reactor, and stirred under 30 bars of CO_2 . The reaction was carried out at 383 K for 6 h. Following the reaction, the 5CC-EBA was precipitated in deionized water to remove NMP and TBAB. The white solid was then filtered and dried under vacuum. After drying, a functionality of two 5CC groups per molecule was determined using 1H NMR spectroscopy (Fig. S1). 1H NMR (400 MHz, DMSO- d_6 ppm): δ = 1.59 (s, 6H), 4.20 (m, 4H), 4.39 (m, 2H), 4.63 (m, 2H), 5.12 (m, 2H), 6.85 (d, 4H), 7.13 (d, 4H).

2.3. Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea (TU)

Synthesis of TU was carried out according to a described procedure [24]. Butylamine (0.81 g, 11.06 mmol) was added dropwise at room temperature to a stirred solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (2.5 g, 9.22 mmol) in anhydrous THF (25 mL). The solution was stirred for 4 h at room temperature. Then, the reaction mixture was concentrated under vacuum and the product was recrystallized from hexane. After drying under vacuum, TU was obtained as a slightly yellow powder (2.97 g, 94 % yield). The structure was confirmed by 1H NMR spectroscopy (Fig. S2). 1H NMR (400 MHz, DMSO- d_6 , ppm): δ = 0.93 (t, 3H), 1.36 (m, 2H), 1.56 (m, 2H), 3.51 (s, 2H), 7.74 (s, 1H), 8.25 (s, 2H), 9.99 (s, NH).

2.4. Synthesis of potassium thioimidate (TU^-)

Synthesis of TU^- was carried out according to a described procedure [36]. TU (17.43 mg, 50.62 μ mol) and potassium methoxide (3.55 mg, 50.62 μ mol) were placed in a dry round bottom flask under argon. Anhydrous THF (10 mL) was then added and the reaction mixture stirred at room temperature for 4 h. THF was then removed under reduced pressure and TU^- was obtained as a yellowish viscous liquid. The structure was confirmed by 1H NMR spectroscopy (Fig. S2). 1H NMR (400 MHz, DMSO- d_6 , ppm): δ = 0.88 (t, 3H), 1.33 (m, 2H), 1.54 (m, 2H), 3.49 (m, 2H), 7.72 (s, 1H), 8.23 (s, 2H).

2.5. NMR spectroscopy procedures

All NMR measurements were performed using a Bruker Advance 400 MHz spectrometer, and the TopSpin software (Bruker, Germany).

2.5.1. Measurement of relaxation times (T_1)

The proton relaxation times (T_1) were measured by an inversion recovery sequence, for both precursors and for the corresponding NIPU. This method is used to determine the time taken for nuclear spins to return to their equilibrium state after being inverted by a radiofrequency pulse. The experiment begins by applying a 180° (π) pulse to the nuclear spins, inverting the longitudinal magnetization. After this pulse, the

spins start to relax and return to their equilibrium state. A variable waiting time called the inversion time (τ_i) is held before applying a 90° ($\pi/2$) pulse, flipping the longitudinal magnetization into the transverse plane (xy-plane). The NMR signal is then detected and, the signal intensity is measured. In order to determine the T_1 for each proton, spectra were acquired at different times τ_i . The experiment was repeated, each time increasing τ_i gradually to produce a series of spectra. All these data were compiled and used to plot the T_1 curve. The relaxation time was equal to the time τ_b divided by $\ln(2)$, where τ_b is the tipping point on the inversion recovery sequence (Fig. S3).

2.5.2. General procedure for kinetic experiments

All kinetic experiments were carried out *in situ* directly in the NMR tube at a 5CC-EBA concentration of 10 mg mL^{-1} in DMSO-d6 at different temperatures. First, 5CC-EBA (10 mg, 0.23 mmol) dissolved in 1 ml of DMSO-d6 was introduced into the tube. The spectrometer was then configured with this tube. After locking on DMSO-d6, magnetic field homogenization (shim), probe adjustment to ^1H core (atma) and signal amplification (rga) were successively performed. Then, 1,4-diaminobutane in stoichiometric conditions (2.06 mg, 0.23 mmol) and the catalyst (from 0 to 0.161 mmol, corresponding to 0.35 eq_{5CC}) solubilized in DMSO-d6, were then added a few seconds before starting the kinetic experiments. The 5CC aminolysis was monitored for 6 h with ^1H NMR spectra acquisition every 5 min, each spectrum being obtained from 16 scans measured with an excitation pulse angle of 67° and a relaxation delay D1 of 3 s. An automatic shimming sequence was used to continuously homogenize the magnetic field during the experiment. After 6h, a ^{13}C NMR spectrum (2048 scans, D1 = 4 s), a DEPT-135° spectrum (1024 scans, D1 = 2 s) and a HSQC 2D spectrum (24 scans, D1 = 1.5 s) were performed to complete the study. Finally, a quantitative ^1H spectrum was also performed (32 scans, D1 = 15 s). The complete NMR sequence is detailed in Table S1.

All NMR signals were integrated using the same integration limits throughout the entire kinetic study, to calculate the corresponding proton concentrations with the TopSpin software. First, the area of the aromatic C and L protons calculated between 7.07 and 7.19 ppm, was used as a reference to calculate the other integrals. This reference area was set at 4, after verifying that the variation of T1 values between C and L did not influence the signal's absolute area during the experiments. Considering the very poor variation ($\leq 0.4\%$) of the absolute area of the C + L signal (Table S2), these aromatic protons were used as an internal reference. Then, the quantitative ^1H spectrum (#113, Table S1) was used to calculate the final concentration of each proton, in the NMR tube. Knowing the initial (#1) and final (#113) concentrations of each proton, the qualitative spectra (#2–109) were used to calculate the consumption of 5CC groups and the formation of carbamate groups, without taking account of T1 variations between protons. Finally, for each spectrum *i*, the aminolysis conversion ratio p_i (Eq. (1)), was calculated from the average integral of the A, B1 and B2 peaks ($[C]_i$), corresponding to the protons carried by the 5CC groups of the 5CC-EBA, and from the hydrolysis ratio ($[H]_i$). The degree of polymerization DPn was calculated from Eq. (3), derived from the Carothers' equation, considering a polyaddition in stoichiometric proportions.

3. Results and discussion

3.1. NMR procedure set-up

3.1.1. Qualitative description of the ^1H NMR spectrum of polymerized NIPU

The linear NIPU polymer studied in the present work was prepared by reaction between commercially available 1,4-diaminobutane and a bis-functional 5-membered cyclic carbonate (5CC-EBA) monomer obtained by DGEBA carbonation. This system has already been reported by Dong et al. with reaction times of 4 h without TBD, or 1h with 30 mol% of TBD, at 298 K [30]. Here, this system was used to investigate the

influence of experimental parameters such as the reaction temperature, or the catalyst type and concentration, on the aminolysis kinetics, using *in situ* NMR spectroscopy.

A NIPU was first synthesized directly in DMSO-d6 at 353 K for 6 h, using 1 eq_{5CC} of diamine and 0.05eq_{5CC} of TBD catalyst. This catalyst concentration (1.3 wt%) was in the range of reported concentrations in NIPU materials (usually between 1 and 6 wt%) [24]. A qualitative ^1H NMR analysis of the NIPU was then performed and compared to the ones of the precursors, in order to attribute the different NMR signals (Fig. S4). The peaks corresponding to the 5CC protons of the 5CC-EBA monomer, visible at 4.39, 4.63 and 5.12 ppm (see A, B1 & B2 protons in ESI, Fig. S1), significantly decreased in the resulting polymer, indicating a consumption of 50.9 % of the 5CC groups during the aminolysis reaction. This was accompanied by the appearance of three new characteristic signals. According to the literature, a first multiplet observed between 3.83 and 4.15 ppm was attributed to the M, O and T methylene protons present on the glycerol-like units containing either a secondary or a primary hydroxyl group and obtained by ring opening of the 5CC, but also to the α -protons N of the secondary hydroxyls [30,37]. Two other peaks at 3.60 ppm (R) and 4.88 ppm (S) were associated with the formation of the primary hydroxyls, with a clear correlation between both signals in COSY (Fig. S5). Nucleophilic addition of the primary amine on the 5CC indeed results in the formation of different isomers due to the possibility of ring opening occurring on either oxygen of the carbonyl group (Fig. 1) [38]. A second reaction corresponding to the partial hydrolysis of cyclic carbonates and the formation of diols was noticed with the appearance of two peaks at 3.48 and 3.79 ppm, attributed to I and J protons of the terminal glycerol-like diols.

3.1.2. Evaluation of the proton relaxation times

In a conventional quantitative NMR experiment, it is generally accepted that the relaxation delay (D1) between each successive excitation pulses must be greater than five times the higher relaxation time (T_1) to ensure complete relaxation of each spin, when a pulse angle of 90° is used [39]. Consequently, the development of a quantitative NMR sequence to determine the aminolysis kinetics of a NIPU formulation under specific conditions, requires the preliminary determination of all T_1 at the temperatures considered. Among the wide variety of experimental methods for measuring T_1 [40], the inversion recovery experiment is clearly the most widely used [41,42]. T_1 was therefore measured at different temperatures between 298 and 353 K, for both precursors (5CC-EBA and 1,4-diaminobutane) and for the synthesized linear NIPU (Table S3). Concerning the precursors first, maximum T_1 values of 3.2 s and 3.4 s were respectively measured at 298 K for the A protons of the 5CC-EBA and the G protons of the diamine, indicating lower mobility than for others protons. Lower T_1 values were then measured when increasing the temperature at 353 K, with minimal T_1 measured at 333 K. For the NIPU protons, lower T_1 values were measured at 298 K, ranging from 0.2 s to 1.9 s. Nevertheless, when increasing the temperature, a different behaviour was observed with a significant increase of the T_1 , to reach up to 5.0 s for the Q protons, corresponding to the methylene in β -position from the nitrogen of the carbamate groups.

Considering this maximum T_1 value of 5.0 s measured for the NIPU formulation in the temperature range investigated, the development of a quantitative NMR sequence would require the application of a relaxation delay D1 of at least 25 s with a pulse angle of 90° , or 5 s with a pulse angle of 67° . Due to this rather long period, it was preferred to work only with qualitative data during the kinetics experiments, using a D1 of 3 s and a pulse angle of 67° , in order to maximise the number of scans for each spectrum but also the number of spectra, and to avoid losing information during the first hour of the experiment. However, since it is possible to study the relative evolution of each peak using qualitative ^1H NMR spectroscopy, it was decided to introduce a quantitative spectrum at the end of each kinetics experiment, in order to recalculate the actual concentration variations for each proton.

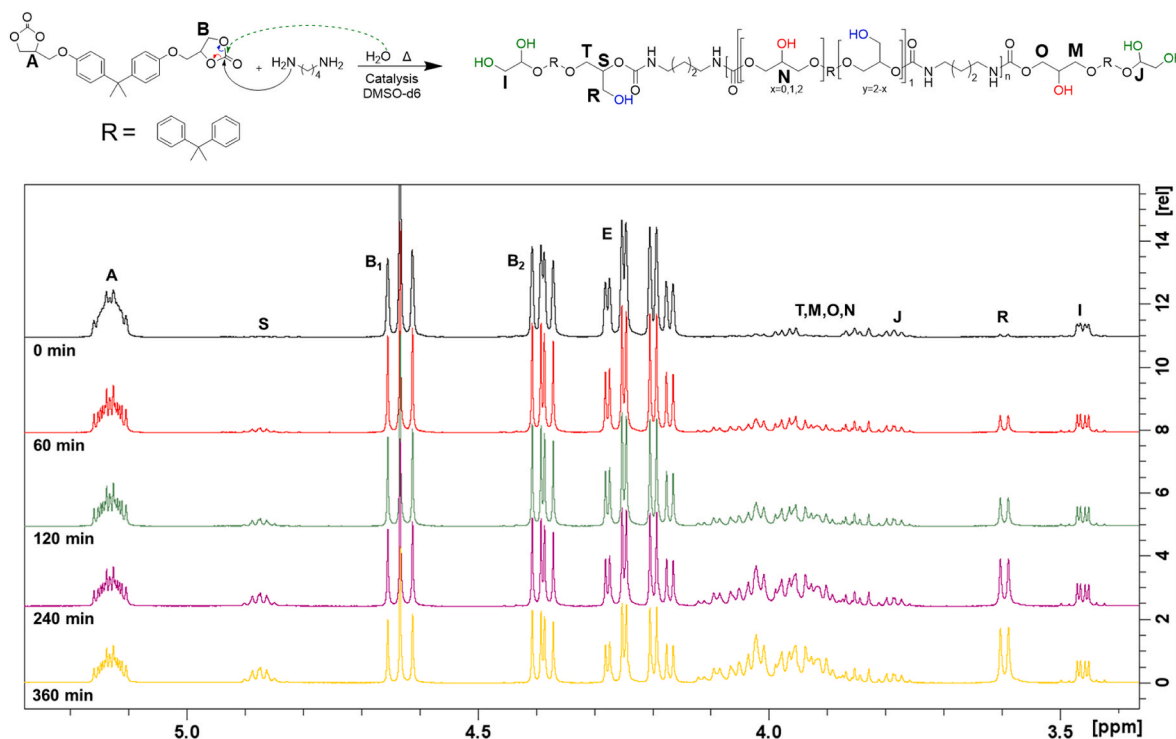


Fig. 1. ^1H NMR spectra between 3.3 and 5.3 ppm obtained *in situ* after 0, 60 min, 120 min, 240 min, 360 min of reaction, in the case of the model reaction between 5CC-EBA and 1,4-diaminobutane, catalysed with TBD (0.05 eq_{5CC}) at 353 K (400 MHz, DMSO- d_6).

3.1.3. NMR experiment configuration for kinetics measurement

Preliminary tests were carried out by introducing both precursors and the catalyst simultaneously in the NMR tube. The tube was then inserted into the spectrometer probe, and pre-acquisition procedures, including locking and shimming, were performed. The disadvantage of this approach was the pre-acquisition delay, resulting in the loss of information during the critical first 7–8 min, which are crucial for investigating the kinetics of reactive formulations. The following tests were consequently carried out by introducing the reagents at different times of the procedure. Initially, only the 5CC-EBA and the DMSO- d_6 were added to the NMR tube, which was then inserted into the spectrometer for pre-acquisition. The NMR tube was then removed from the spectrometer, before adding the amine and catalyst. After mixing, the tube was reinserted into the spectrometer, and spectrum acquisition started without further pre-acquisition. Nevertheless, during the reaction, the chemical composition inside the NMR tube evolved due to the consumption of both precursors and the progressive synthesis of the NIPU, disturbing the magnetic field. As a result, the spectral resolution decreased as the reaction progressed. To overcome this problem, an automatic shimming process was used throughout the entire reaction. The spectrometer adjusted the shim settings before each acquisition to adjust and homogenize the magnetic field, ensuring consistent spectral quality.

3.2. Aminolysis kinetics of 5CC-EBA with TBD at 353 K

The *in situ* NMR methodology was then used to investigate the aminolysis kinetics of a first formulation constituted of 5CC-EBA, 1.0 eq_{5CC} of diamine and 0.05eq_{5CC} of TBD catalyst. The progressive conversion of both 5CC and amine groups was monitored at 353 K as a function of time between 0 min and 360 min. Indeed, the *in situ* monitoring of the 5CC-EBA aminolysis allowed the visualization of the progressive consumption of the 5CC groups and the formation of the carbamate groups, during the 6 h of experiment (Fig. 1). First, the 3 signals corresponding to the protons A (5.12 ppm) and B (4.63 and 4.39

ppm) of the 5CC rings continuously decreased, to reach a conversion ratio of 50.9 % and an aminolysis ratio of 43.1 % after 6h of reaction (Fig. 2). The disappearance of the multiplet between 3.83 and 4.15 ppm, corresponding to the multiplet of the protons M, N, O and T, carried by the glycerol-like units formed by aminolysis and ring opening of the 5CC. Both additional signals at 3.60 (R) and 4.88 ppm (S) corresponding to the protons of the opened 5CC units containing a primary hydroxyl, were also progressively increasing. Using the quantitative spectrum measured at the end of the experiment, it was possible to calculate the concentration evolution of each proton during the *in situ* monitoring. After 6h, the relative abundance of primary hydroxyl groups in the final NIPU polymer was determined from the signals at 3.60 and 4.88 ppm. The proportion of secondary hydroxyls was then deduced from this calculation as it was not possible to

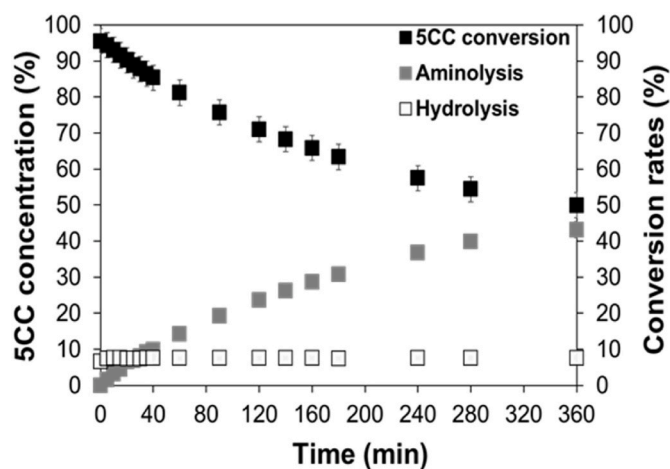


Fig. 2. Evolution of the 5CC concentrations and of the aminolysis and hydrolysis ratios during the *in situ* monitoring of the NIPU formation in the presence of TBD (0.05 eq_{5CC}) during 6h at 353 K.

accurately determine the α -proton integral (N) of secondary hydroxyls in the multiplet. Proportions of primary and secondary hydroxyl groups of 33 % and 67 % were calculated, respectively. This result indicated that in these conditions, ring opening of the 5CC groups preferentially occurred on the oxygen bonded to the 5CC asymmetric carbon, in good agreement with previous studies [43,44].

Nevertheless, partial hydrolysis of the 5CC groups to end-chain diols was also observed, with signals appearing at 3.48 (I) and 3.79 ppm (J). After 6 h, the proportion of hydrolysed 5CC was approximately 7.5 % of the initial 5CC concentration, suggesting that the hydrolysis reaction remained a minor pathway compared to the aminolysis reaction (Fig. 2). Nevertheless, 74 % of the hydrolysis occurred during the first 5 min of the experiment, and only 2.1 % of the initial 5CC were hydrolysed between 5 and 360 min. The rapid hydrolysis observed at the experiment beginning, could be attributed to the presence of a small amount of water (~ 0.44 g/L) even in anhydrous DMSO-d₆, or to residual moisture in the atmosphere during tube preparation. Very interestingly, the disappearance of 5CC groups, were clearly correlated to the appearance of the multiplet ($R^2 = 0.999$), with a slope of 0.94, indicating that most of the converted 5CC groups were involved in the NIPU synthesis, limiting the influence of side reactions at 353 K (Fig. 3). The difference of 6 % between this slope and a theoretical value of 1, was of the same order than the hydrolysis ratio (7.5 %) measured in this experiment, indicating that no additional secondary reaction occurred.

3.3. Influence of TBD catalyst concentration on the aminolysis kinetics of 5CC-EBA

The developed NMR sequence was then used to investigate the influence of the TBD concentration on the reaction kinetics, at 353 K. Different experiments were carried out using TBD concentrations ranging from 0 to 0.35 eq_{5CC}, in good agreement with the catalyst concentrations reported in the literature [24]. In these experiments, the formation of the urethane compound was monitored by the appearance of the multiplet between 3.83 and 4.15 ppm. The influence of the catalyst concentration on the aminolysis kinetics was clearly observed (Table 1). Indeed, NIPU formation progressed more rapidly when the TBD concentration was increased. As a consequence, the final aminolysis ratio after 6h was between 17.3 % and 87.5 %, depending on the TBD concentration (Fig. 4A). The hydrolysis kinetics also depended on the catalyst concentration as the final hydrolysis ratio of 5CC groups ranged from 5.8 % with no TBD, up to 14 % with 0.15 eq_{5CC}. The initial hydrolysis ratios were observed to range from 5 % without catalyst to 8.2 % with 0.35 eq_{5CC} (Fig. 4B). By increasing the amount of TBD, the

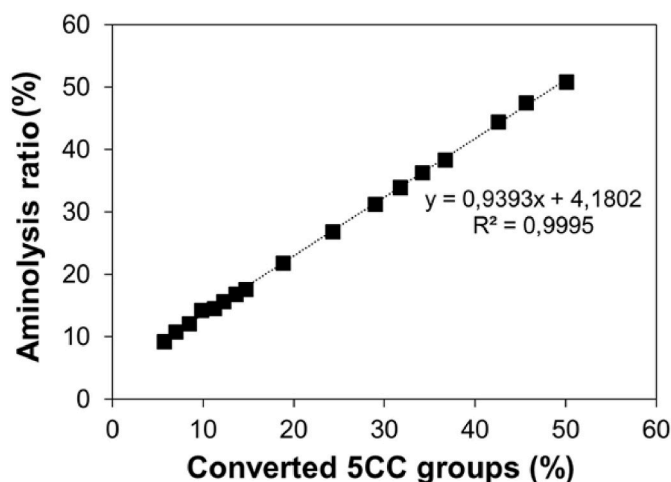


Fig. 3. Evolution of the carbamate group concentration with the proportion of converted 5CC groups, during the *in situ* monitoring of the NIPU formation in the presence of TBD (0.05 eq_{5CC}) during 6h at 353 K.

hydrolysis mechanism appears to compete with the aminolysis mechanism. Actually, in its protonated form, HTBD⁺ could favour the activation of the 5CC carbonyl, at the expense of the amine activation [19,45].

The proportion of primary and secondary hydroxyls in the NIPU structure was also determined after 6h of reaction. A relative proportion ranging from 65 % to 78 % was calculated for secondary hydroxyls, showing no specific trend between each TBD concentration (Table 1). Considering these results, the catalyst concentration did not show any significant effect on the isomer proportions, with a mean proportion of secondary hydroxyls of (72 ± 6) %.

To mimic the specifications of industrial PU formulations, a catalyst concentration lower than 2 wt% is expected. In the following sections, it was therefore decided to use a catalyst concentration of 0.07 eq_{5CC}, corresponding to 1.8 wt%, in order to optimize the aminolysis kinetics.

3.4. Influence of the temperature on the reaction kinetics in presence of TBD

3.4.1. 5CC conversion ratios depending on the experiment temperature

The effect of the temperature on the kinetics of the aminolysis and hydrolysis reactions was then investigated. Reactions were carried out using 0.07 eq_{5CC} at temperatures between 298 K and 353 K, to avoid secondary reactions [9]. The conversion of 5CC groups was monitored as a function of time between 0 min and 360 min, by studying the relative disappearance of the NMR signals at 4.39, 4.63 and 5.12 ppm (Fig. 5B). The evolution of the corresponding curves clearly shows an influence of the reaction temperature on the kinetics of 5CC consumption (Fig. 5A). As expected, increasing the reaction temperature significantly accelerated the aminolysis reaction, with aminolysis ratios ranging between 15.8 % and 67.0 % for reaction temperatures of 298 K and 353 K, respectively (Fig. 5B). However, the lower the reaction temperature, the greater the effect of an increase of just a few degrees. Indeed, for the reaction studied, the effect of temperature on the aminolysis reaction was found to be minimal between 333 K and 353 K. Both kinetic curves showed no significant variation during the first hour of reaction, but different aminolysis ratios of 58.9 % and 67.0 % were measured after 6h at 333 K and 353 K, respectively.

Partial hydrolysis of the 5CC was also observed, with the appearance of the peaks at 3.48 and 3.79 ppm. Nevertheless, most of the hydrolysis took place during the initial 5 min of the reaction, with observed ratios fluctuating between 6.1 % and 8.0 %. Final hydrolysis ratios were between 7.7 % and 8.7 % (Table 1), indicating that temperature had a much lower impact than the TBD concentration. Moreover, increasing the reaction temperature had no significant influence on the proportions of both isomers formed by ring opening of the 5CC. Indeed, a mean relative proportion of (67 ± 5) % was calculated for the secondary hydroxyl groups, with no specific trend depending on the temperature.

3.4.2. Calculation of the activation energy of the aminolysis reaction

The aminolysis of 5-membered bis-cyclic carbonates generally follows second-order kinetics when stoichiometric proportions of 5CC and amine groups are considered [15,46]. In this study, the aminolysis reaction was assumed to follow the polymerization kinetics equations for a linear system with an external catalyst (Equations (1)–(3)). Considering the hydrolysis reaction, the rate constant of the aminolysis reaction (k_{Am}) was calculated from the slope of the linear regression ($R^2 > 0.99$) between the degree of polymerization (DP_n) and time (Fig. 6), for each investigated reaction temperature (Table 1).

$$p_i = \frac{\Delta[C]_0 - \Delta[C]}{[C]_0} = \frac{([C]_0 - [H]_0) - ([C]_i - [H]_i)}{[C]_0 - [H]_0} \quad (\text{Eq.1})$$

$$DP_n = \frac{1}{1 - p_i} = \frac{1}{1 - \frac{([C]_0 - [H]_0) - ([C]_i - [H]_i)}{[C]_0 - [H]_0}} = \frac{[C]_0 - [H]_0}{[C]_i - [H]_i} \quad (\text{Eq.2})$$

Table 1

Influence of the concentration of TBD catalyst and of the temperature reaction, on the aminolysis and hydrolysis ratios and on the NIPU structure, measured after 6h by *in situ* NMR monitoring of the reaction of 5CC-EBA and 1,4-diaminobutane (DMSO-d₆, 400 MHz).

Entry	Concentration of TBD ^a (eq _{5CC})	Reaction temperature (K)	Final aminolysis ratio of 5CC (mol%)	Final hydrolysis ratio of 5CC (mol%)	Isomer ratio ^b OH _{II} : OH _I	Aminolysis kinetics constant k _{Am} ^c (L.mol ⁻¹ .min ⁻¹)
1	–	353	17.3	5.8	0.65 : 0.35	3.16x10 ⁻⁵
2	0.050	353	43.1	7.5	0.67 : 0.33	1.39x10 ⁻³
3	0.070	353	67.0	7.6	0.78 : 0.22	5.77x10 ⁻³
4	0.15	353	74.5	14	0.78 : 0.22	1.96x10 ⁻²
5	0.35	353	87.5	13	0.73 : 0.27	6.34x10 ⁻²
6	0.070	298	15.8	7.7	0.65 : 0.35	9.18x10 ⁻⁴
7	0.070	313	49.5	7.7	0.62 : 0.38	2.15x10 ⁻³
8	0.070	333	58.9	8.7	0.73 : 0.27	4.74x10 ⁻³

^a TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

^b OH_{II} and OH_I: secondary and primary hydroxyl groups of both isomers obtained by 5CC ring opening.

^c Calculated from Eq. (3).

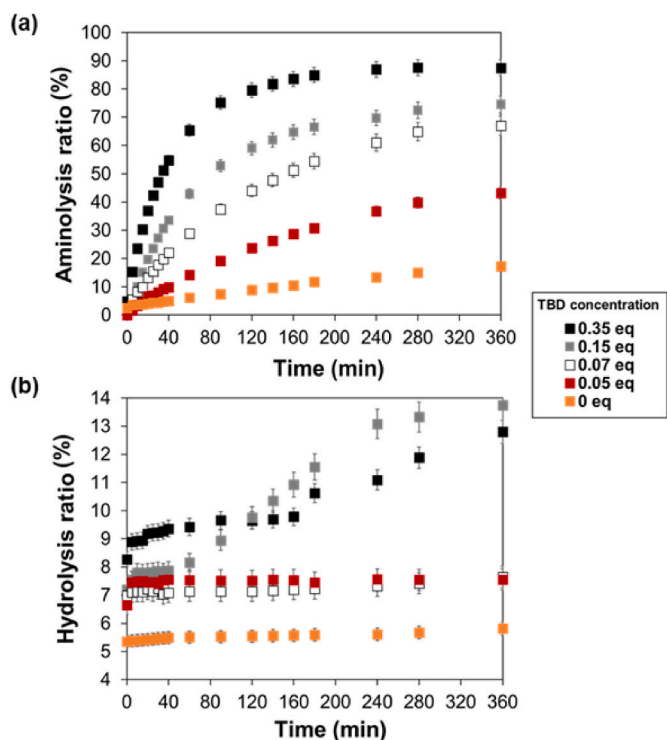


Fig. 4. (a) Evolution of the aminolysis and (b) hydrolysis ratios in the reaction of 2,2-bis[p-(1,3-dioxolan-2-one-4-ylmethoxy)phenyl] and 1,4-diaminobutane at 353 K in the presence of TBD concentrations between 0 and 0.35 eq_{5CC}, measured by *in situ* NMR spectroscopy (DMSO-d₆, 400 MHz).

$$DP_n = ([C]_0 - [H]_0) k_{Am} t + 1 \quad (\text{Eq.3})$$

where $[C]_0$ and $[H]_0$ are the concentrations of 5CC groups and hydrolysed diols at the experiment start, and $[C]_i$ and $[H]_i$ are the concentrations of 5CC groups and hydrolysed diols determined by the NMR method at the considered reaction time i . pi and DP_n represent the conversion ratio and degree of polymerization of the aminolysis reaction.

Most studies dealing with aminolysis kinetics stopped after estimating the rate constant [15]. To the best of our knowledge, only one publication detailed a kinetic study of NIPU synthesis, extending to the determination of activation energies [47]. In this paper, Yuen et al. carried out a kinetic study on monofunctional cyclic carbonates with 5- and 8-membered rings in the presence of five different amines. The activation energy for 8-membered was estimated at 40 kJ mol⁻¹,

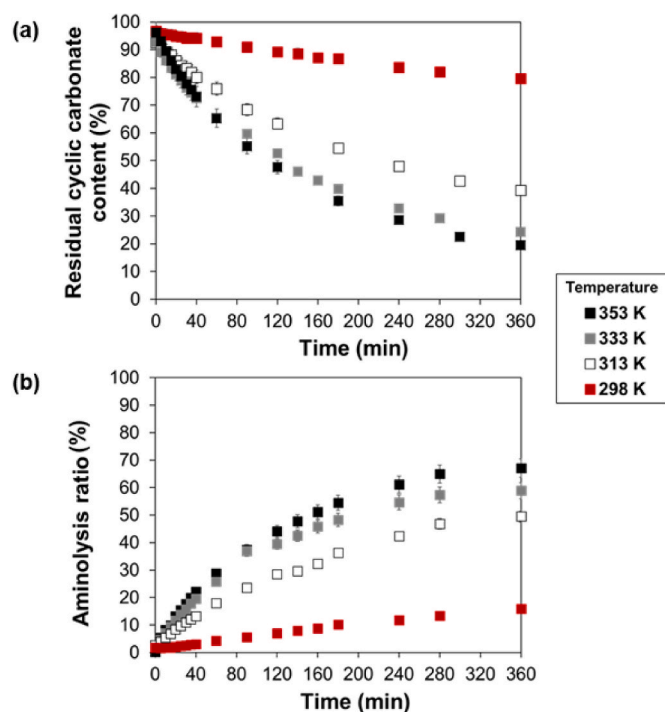


Fig. 5. Evolution of the (a) residual cyclic carbonate content and of the (b) aminolysis ratio during the reaction of 2,2-bis[p-(1,3-dioxolan-2-one-4-ylmethoxy)phenyl] and 1,4-diaminobutane, catalysed with TBD (0.07 eq_{5CC}), measured by *in situ* NMR spectroscopy (DMSO-d₆, 400 MHz).

whereas the activation energy was not determined for their 5CC precursor. Activation energies (E_a) can be estimated from the aminolysis rate constant (k_{Am}), using Arrhenius' law (Equation (4)).

$$k_{Am} = A e^{-\frac{E_a}{RT}} \quad (\text{Eq.4})$$

where k_{Am} is the aminolysis rate constant, R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the reaction temperature (in K) and A is the pre-exponential factor representing the frequency of collisions between the reactive molecules. E_a and A were determined by plotting the evolution of $\ln(k_{Am})$ with $1/RT$ (in J.mol⁻¹; Fig. 7). Thus, an activation energy of 29.7 kJ mol⁻¹ and a pre-exponential factor A of 175.7 L mol⁻¹.min⁻¹ were calculated for the TBD catalyst (Table 2).

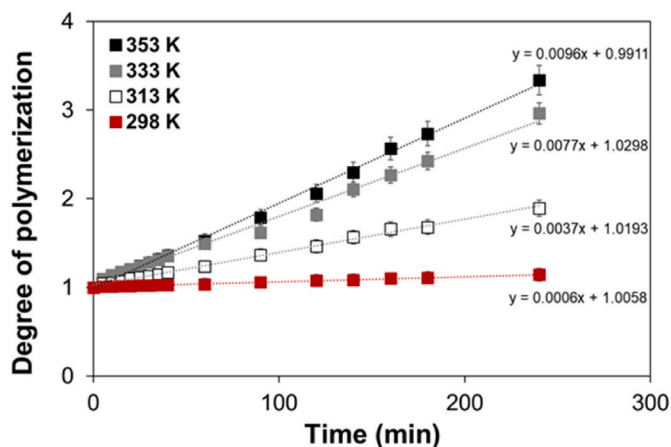


Fig. 6. Evolution of the calculated degree of polymerization (DPn) during the reaction of 5CC-EBA with 1,4-diaminobutane catalysed with TBD (0.07 eq_{5CC}) at temperatures of 298, 313, 333 and 353 K.

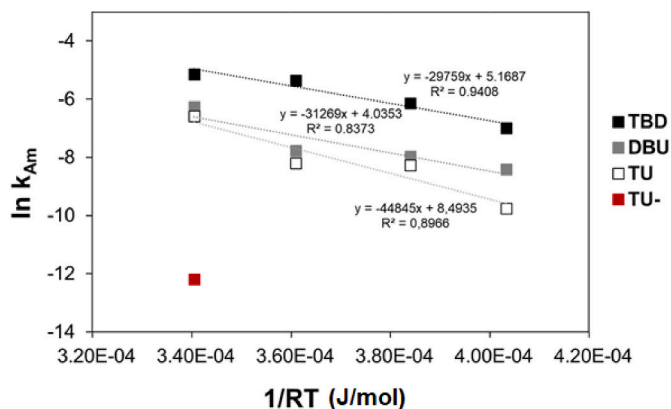


Fig. 7. Relationship between $\ln(k_{Am})$ and $1/RT$ during the reaction of 5CC-EBA with 1,4-diaminobutane catalysed with 0.07 eq_{5CC} TBD, DBU, TU or TU⁻ in DMSO-d₆.

3.5. Influence of the catalyst nature on the aminolysis kinetics of 5CC-EBA

3.5.1. Qualitative description of the catalyst effect

The NMR methodology was finally used to study the influence of the catalyst nature on the kinetics of the aminolysis and hydrolysis reactions at temperatures between 298 and 353 K. The reaction was carried out using 5CC-EBA and 1,4-diaminobutane in stoichiometric conditions, and 0.07 eq_{5CC} of a given catalyst. The evolution of the 5CC and carbamate concentrations clearly shows an influence of the catalyst structure on the reaction kinetics (Fig. 8A). TBD proved to be the most efficient catalyst, with an aminolysis ratio of 67.0 % after 6 h at 353 K, compared with

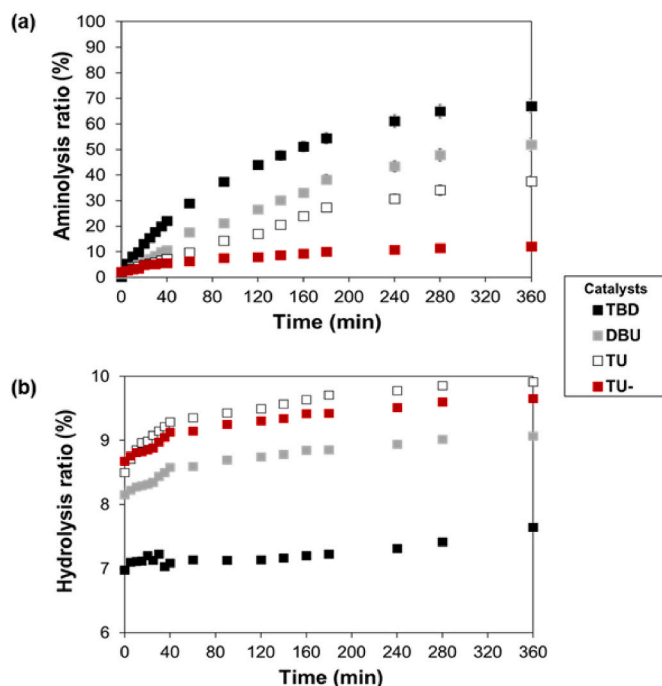


Fig. 8. Evolution of the (a) aminolysis and (b) hydrolysis ratios during the reaction of 2,2-bis[p-(1,3-dioxolan-2-one-4-ylmethoxy)phenyl] and 1,4-diaminobutane, catalysed with 0.07 eq_{5CC} TBD, DBU, TU or TU⁻ at 353 K.

Table 2

Aminolysis and hydrolysis final ratios, isomer proportions in the final NIPU structure, and kinetic parameters of the aminolysis reaction, depending on the catalyst at temperatures between 298 and 353 K.

Entry	Catalysts ^a	Reaction temperature	Final aminolysis ratio of 5CC	Final hydrolysis ratio of 5CC	Isomer ratio ^b OH _{II} : OH _I	Aminolysis kinetics constant k_{Am} ^c	E_a ^d	A ^d
		(K)	(mol%)	(mol%)		(L.mol ⁻¹ .min ⁻¹)		
1	TBD	298	15.8	7.7	0.65 : 0.35	9.18×10^{-4}	29.7	176
		313	49.5	7.7	0.62 : 0.38	2.15×10^{-3}		
		333	58.9	8.7	0.73 : 0.27	4.74×10^{-3}		
		353	67.0	7.6	0.78 : 0.22	5.76×10^{-3}		
2	DBU	298	16.9	7.9	0.74 : 0.26	2.23×10^{-4}	31.2	56.6
		313	24.2	7.1	0.79 : 0.21	3.43×10^{-4}		
		333	30.1	7.8	0.83 : 0.17	4.20×10^{-4}		
		353	51.9	9.0	0.85 : 0.15	1.91×10^{-3}		
3	TU	298	18.1	8.6	0.83 : 0.17	5.78×10^{-5}	44.8	4880
		313	19.5	8.7	0.79 : 0.21	2.57×10^{-4}		
		333	21.2	8.5	0.81 : 0.19	2.77×10^{-4}		
		353	37.5	9.9	0.84 : 0.16	1.37×10^{-3}		
4	TU ⁻	353	12.1	9.6	0.64 : 0.36	5.07×10^{-6}	n.d.	n.d.

^a DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; TBD: 1,5,7-triazabicyclo[4.4.0]dec-5-ene; TU: 1-(3,5-bis(trifluoromethyl)phenyl)-3-butylthiourea.

^b OH_{II} and OH_I: secondary and primary hydroxyl groups of both isomers obtained by 5CC ring opening.

^c Calculated from Eq. (3).

^d Calculated from Eq. 4.

12.1 % for TU⁻, 37.5 % for TU and 51.9 % for DBU. All the results are quite logical when comparing the morphology of each catalyst. TU and DBU catalysts only interact with either the amine or the cyclic carbonate. In contrast, TBD acts as a dual-activation catalyst [48], due to its strong basicity (pKa = 26 in acetonitrile) [45,49]. It interacts simultaneously with both the amine and the cyclic carbonate precursors through hydrogen bonding. For the thiourea-based catalysts, TU and TU⁻, a significant difference in reactivity was observed. Surprisingly, the results with thiourea based catalysts were in complete contrast to the literature. Indeed, Blain et al. and Bossion et al. demonstrated the high efficiency of these catalysts in aminolysis reactions [24,50]. For the TU⁻ catalyst, they achieved a conversion ratio of over 90 % at 393 K under bulk synthesis conditions. These good results were explained by a bifunctional mechanism proposed by Lin and Waymouth, suggesting that TU⁻ can activate both cyclic carbonates and diamines [51]. Nevertheless, TU⁻ was found to be inefficient for our system, and was therefore removed from the study. The poor results could be due to the instability of the anionic form in DMSO-d6. It has also been demonstrated that cyclohexylphenyl-based thiourea can outperform TBD at low catalyst loading, indicating that the concentration of this catalyst appears to be a crucial parameter [52].

Concerning the influence of the catalyst nature on the PHU structure, the relative abundance of each isomer was determined from the signals at 3.60 ppm and 4.88 ppm (Table 2). Irrespective of the catalyst used, secondary alcohols were favoured with relative proportions greater than 64 % (TU⁻) and up to 85 % (DBU). Considering this difference, the nature of the catalyst was supposed to have an influence on the proportions of primary and secondary hydroxyls. On the other hand, 5CC hydrolysis ratios ranging from 6.8 % to 8.6 % after 5 min at 353 K, and from 7.6 % to 9.9 % after 6 h, were also measured (Fig. 8B). Consequently, the catalyst nature did not show a significant influence on the 5CC hydrolysis kinetics.

3.5.2. Polymerization kinetics

As performed for TBD catalyst, the aminolysis rate constant (k_{Am}), the activation energy (E_a) and the pre-exponential factor A, were calculated using Equations 3-4, for the NIPU systems containing either the DBU or the TU catalyst (Table 2). The TU⁻ catalyst was excluded from the study due to its inadequate kinetic performance at 353 K.

As explained above, the frequency factor A in the Arrhenius equation represents the frequency of collisions between reactants in a chemical reaction. This constant can be used to estimate the nature and probability of the reaction between the precursors. By comparing the value of A for each catalyst, it is also possible to determine which reaction is the most efficient. It also provides insights into the rate and mechanism of the reaction under different conditions, such as temperature and catalyst concentration. The frequency factor A was determined for the three catalytic systems, revealing that TU exhibited the highest frequency factor among them (4880 L mol⁻¹.min⁻¹ for TU vs 176 L mol⁻¹.min⁻¹ for TBD). Consequently, at high temperature, TU is expected to be more efficient than TBD and DBU. Nevertheless, at temperatures lower than 373 K allowing the avoidance of side reactions, the TBD-catalysed reaction, for which an E_a value of 29.7 kJ mol⁻¹ was calculated, was the most favoured in our experimental conditions. Thus, TBD showed a higher catalytic efficiency than other catalysts between 298 and 353 K. Consequently, at 353 K, the aminolysis ratio constants of TBD were three times higher (5.76x10⁻³ L mol⁻¹.min⁻¹) than that of DBU (1.91x10⁻³ L mol⁻¹.min⁻¹), underlining the promising potential of future catalysts based on this guanidine-type structure.

Studies have shown that temperature has a little effect on the hydroxyl ratio [13,53,54]. This catalyst screening also confirms the relatively small effect of the DBU, TBD and TU catalysts on the hydroxyl ratio. Actually, previous studies have showed that the most important factors influencing the regioselectivity of aminolysis appears to be the structural configuration of the precursors [55,56]. On the other hand, the nature of the potential solvent appears to be one of the least

important factors influencing the regioselectivity of aminolysis [53,54]. However, the choice of solvent can significantly impact the aminolysis kinetics [15]. Furthermore, using our NMR method for characterization of reaction kinetics in the solvent route, it is clear that aminolysis kinetics depend on the concentration of the reagents. Thus, the selectivity of the 5CC aminolysis reaction remains a subject of study. It is not yet fully controlled, but can nevertheless be used to synthesise NIPU with controlled structures.

This NMR method allowed a rapid understanding of the reactivity of the precursors under different conditions (temperature, catalysts, catalyst concentrations, etc.). It also allowed a precise elucidation of the microstructure of the final NIPU and how it is influenced by the different parameters. This approach will make it possible to better control the structure of NIPUs and to establish structure-properties relationships which are important for potential applications. A further advantage is the possibility of rapid screening of aminolysis conditions, which avoids the need for experiments that are costly in terms of infrastructure and raw materials. On the other hand, the significant influence of TBD on reactivity was also confirmed by this *in situ* method. The results are in agreement with those reported in the literature, thus validating the NMR approach used in this study. Consequently, this reliable *in situ* NMR method is paving the way for the rapid screening of innovative (co-) catalysts in order to improve the aminolysis kinetics of sustainable NIPUs.

4. Conclusions

The effect of the catalyst nature and concentration as well as the reaction temperature on the polymerization kinetics of a non-isocyanate polyurethane (NIPU) was fully investigated, using a reliable *in situ* characterization method based on NMR spectroscopy. The aim was to identify the most favorable conditions to accelerate the aminolysis of a bis-functional 5-membered cyclic carbonate. Solution-state NMR was consequently used to perform a complete kinetic study of the aminolysis reaction. The *in situ* monitoring of the reactions provided a comprehensive approach for studying various aspects of NIPU synthesis, including the characterization of potential side reactions kinetics and by-products, the aminolysis kinetic parameters, and the isomer distributions in the final NIPU structure. The knowledge gained from such analyses contributes significantly to our understanding of NIPU synthesis processes and has great potential for further research. In summary, this study has led to the development of a comprehensive and reliable methodology that is now ready to be used in the identification and discovery of new catalysts for the synthesis of next-generation NIPUs with improved reactivity.

CRedit authorship contribution statement

Anthony Monmagnon: Writing – original draft, Methodology, Investigation, Conceptualization. **Pierre-Alain Bayle:** Methodology, Investigation. **Florence Flaig:** Project administration, Funding acquisition. **Céline Carpe:** Project administration, Funding acquisition. **Jaouad El Harfi:** Project administration, Funding acquisition. **Renaud Demadrille:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Sébastien Rolere:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2024.108615>.

Data availability

Data will be made available on request.

References

- Plastics - the facts 2020 • plastics europe. <https://plasticseurope.org/knowledge-hub/plastics-the-facts-2020/>. (Accessed 30 August 2022).
- B.-X. Cheng, W.-C. Gao, X.-M. Ren, X.-Y. Ouyang, Y. Zhao, H. Zhao, W. Wu, C.-X. Huang, Y. Liu, X.-Y. Liu, H.-N. Li, R.K.Y. Li, A review of microphase separation of polyurethane: characterization and applications, *Polym. Test.* 107 (2022) 107489, <https://doi.org/10.1016/j.polymertesting.2022.107489>.
- S.D. Bote, A. Kiziltas, I. Scheper, D. Milewski, R. Narayan, Biobased flexible polyurethane foams manufactured from lactide-based polyester-ether polyols for automotive applications, *J. Appl. Polym. Sci.* 138 (2021) 50690, <https://doi.org/10.1002/app.50690>.
- A. Tenorio-Alfonso, M.C. Sánchez, J.M. Franco, A review of the sustainable approaches in the production of bio-based polyurethanes and their applications in the adhesive field, *J. Polym. Environ.* 28 (2020) 749–774, <https://doi.org/10.1007/s10924-020-01659-1>.
- J.O. Akindoyo, M.D.H. Beg, S. Ghazali, M.R. Islam, N. Jeyaratnam, A.R. Yuvaraj, Polyurethane types, synthesis and applications – a review, *RSC Adv.* 6 (2016) 114453–114482, <https://doi.org/10.1039/C6RA14525F>.
- A. Gomez-Lopez, F. Elizalde, I. Calvo, H. Sardon, Trends in non-isocyanate polyurethane (NIPU) development, *Chem. Commun.* (2021) 12254–12265, <https://doi.org/10.1039/D1CC00509E>.
- S. El Khezraji, H. Benyoucef, L. Belachemi, M.A. Lopez Manchado, R. Verdejo, M. Lahcini, Recent progress of non-isocyanate polyurethane foam and their challenges, *Polymers* 15 (2023) 254, <https://doi.org/10.3390/polym15020254>.
- H. Wu, D. Liao, X. Chen, G. Du, T. Li, H. Essawy, A. Pizzi, X. Zhou, Functionalized Natural Tannins for Preparation of a novel non-isocyanate polyurea-based adhesive, *Polym. Test.* 117 (2023) 107853, <https://doi.org/10.1016/j.polymertesting.2022.107853>.
- A. Cornille, R. Auvergne, O. Figovsky, B. Boutevin, S. Caillol, A perspective approach to sustainable routes for non-isocyanate polyurethanes, *Eur. Polym. J.* 87 (2017) 535–552, <https://doi.org/10.1016/j.eurpolymj.2016.11.027>.
- M. Blain, A. Cornille, B. Boutevin, R. Auvergne, D. Benazet, B. Andrioletti, S. Caillol, Hydrogen bonds prevent obtaining high molar mass PHUs, *J. Appl. Polym. Sci.* 134 (2017) 44958, <https://doi.org/10.1002/app.44958>.
- F. Magliozzi, Synthèse de polyhydroxyuréthanes biosourcés par extrusion réactive: élaboration de matériaux aux propriétés originales, Université de Bordeaux, 2019. PhD thesis, <https://tel.archives-ouvertes.fr/tel-02890242>.
- H. Tomita, F. Sanda, T. Endo, Polyaddition of bis(seven-membered cyclic carbonate) with diamines: a novel and efficient synthetic method for polyhydroxyurethanes, *J. Polym. Sci. Polym. Chem.* 39 (2001) 4091–4100, <https://doi.org/10.1002/pola.10058>.
- H. Tomita, F. Sanda, T. Endo, Polyaddition behavior of bis(five- and six-membered cyclic carbonate)s with diamine, *J. Polym. Sci. Polym. Chem.* 39 (2001) 860–867, [https://doi.org/10.1002/1099-0518\(20010315\)39:6<860::AID-POLA1059>3.0.CO;2-2](https://doi.org/10.1002/1099-0518(20010315)39:6<860::AID-POLA1059>3.0.CO;2-2).
- G. Coste, D. Berne, V. Ladmiraal, C. Negrell, S. Caillol, Non-isocyanate polyurethane foams based on six-membered cyclic carbonates, *Eur. Polym. J.* 176 (2022) 111392, <https://doi.org/10.1016/j.eurpolymj.2022.111392>.
- A. Cornille, M. Blain, R. Auvergne, B. Andrioletti, B. Boutevin, S. Caillol, A study of cyclic carbonate aminolysis at room temperature: effect of cyclic carbonate structures and solvents on polyhydroxyurethane synthesis, *Polym. Chem.* 8 (2017) 592–604, <https://doi.org/10.1039/C6PY01854H>.
- B. Quienne, R. Poli, J. Pinaud, S. Caillol, Enhanced aminolysis of cyclic carbonates by β -hydroxylamines for the production of fully biobased polyhydroxyurethanes, *Green Chem.* 23 (2021) 1678–1690, <https://doi.org/10.1039/D0GC04120C>.
- D. Berne, G. Coste, R. Morales-Cerrada, M. Boursier, J. Pinaud, V. Ladmiraal, S. Caillol, Taking advantage of β -hydroxy amine enhanced reactivity and functionality for the synthesis of dual covalent adaptable networks, *Polym. Chem.* 13 (2022) 3806–3814, <https://doi.org/10.1039/D2PY00274D>.
- M. Blain, H. Yau, L. Jean-Gérard, R. Auvergne, D. Benazet, P.R. Schreiner, S. Caillol, B. Andrioletti, Urea- and thiourea-catalyzed aminolysis of carbonates, *ChemSusChem* 9 (2016) 2269–2272, <https://doi.org/10.1002/cssc.201600778>.
- J.G. Kim, G.S. Lee, A. Lee, Triazabicyclodecane: a versatile catalyst for polymer synthesis, *J. Polym. Sci.* 62 (2024) 42–91, <https://doi.org/10.1002/pol.20230643>.
- E. Fritz-Langhals, Unique superbase TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene): from catalytic activity and one-pot synthesis to broader application in industrial chemistry, *Org. Process Res. Dev.* 26 (2022) 3015–3023, <https://doi.org/10.1021/acs.oprd.2c00248>.
- T.R. Puleo, S.J. Sujansky, S.E. Wright, J.S. Bandar, Organic superbases in recent synthetic methodology research, *Chem. Eur. J.* 27 (2021) 4216–4229, <https://doi.org/10.1002/chem.202003580>.
- M.K. Kiesewetter, M.D. Scholten, N. Kirn, R.L. Weber, J.L. Hedrick, R. M. Waymouth, Cyclic guanidine organic catalysts: what is magic about triazabicyclodecane? *J. Org. Chem.* 74 (2009) 9490–9496, <https://doi.org/10.1021/jo902369g>.
- R.H. Lambeth, T.J. Henderson, Organocatalytic synthesis of (poly) hydroxyurethanes from cyclic carbonates and amines, *Polymer* 54 (2013) 5568–5573, <https://doi.org/10.1016/j.polymer.2013.08.053>.
- M. Blain, L. Jean-Gérard, R. Auvergne, D. Benazet, S. Caillol, B. Andrioletti, Rational investigations in the ring opening of cyclic carbonates by amines, *Green Chem.* 16 (2014) 4286–4291, <https://doi.org/10.1039/C4GC01032A>.
- F. Lagarde, Nouveaux catalyseurs confinés pour la valorisation du CO₂, Ecole Centrale Marseille, France, 2018. PhD thesis, <https://theses.hal.science/tel-02103764>.
- M. Bourguignon, B. Grignard, C. Detrembleur, Cascade exotherms for rapidly producing hybrid nonisocyanate polyurethane foams from room temperature formulations, *J. Am. Chem. Soc.* 146 (2024) 988–1000, <https://doi.org/10.1021/jacs.3c11637>.
- N.S. Purwanto, Y. Chen, T. Wang, J.M. Torkelson, Rapidly synthesized, self-blowing, non-isocyanate polyurethane network foams with reprocessing to bulk networks via hydroxyurethane dynamic chemistry, *Polymer* 272 (2023) 125858, <https://doi.org/10.1016/j.polymer.2023.125858>.
- A. Bossion, New Challenges in the Synthesis of Non-isocyanate Polyurethanes, Université de Bordeaux; Universidad del País Vasco, 2018. PhD thesis, <https://tel.archives-ouvertes.fr/tel-01998058>.
- V. Valette, N. Kébir, F.B. Tiavarison, F. Burel, L. Lecamp, Preparation of flexible biobased non-isocyanate polyurethane (NIPU) foams using the transurethanization approach, *React. Funct. Polym.* 181 (2022) 105416, <https://doi.org/10.1016/j.reactfunctpolym.2022.105416>.
- W. Dong, Y. Yoshida, T. Endo, Synthesis of poly(hydroxyurethane) from 5-membered cyclic carbonate under mild conditions in the presence of bicyclic guanidine and their reaction process, *J. Polym. Sci.* 59 (2021) 502–509, <https://doi.org/10.1002/pol.20200825>.
- M. Kamigaito, Y. Maeda, M. Sawamoto, T. Higashimura, Living cationic polymerization of isobutyl vinyl ether by hydrogen chloride/Lewis acid initiating systems in the presence of salts: in-situ direct NMR analysis of the growing species, *Macromolecules* 26 (1993) 1643–1649, <https://doi.org/10.1021/ma00059a023>.
- M. Sawamoto, The nature of the growing species in living cationic polymerization: principles, stereochemistry, and in-situ NMR analysis, *Macromol. Symp.* 85 (1994) 33–43, <https://doi.org/10.1002/masy.19940850104>.
- E. Rodrigues, P. Sebastião, M.I. Tavares, ¹H Time Domain NMR real time monitoring of polyacrylamide hydrogels synthesis, *Polym. Test.* 60 (2017), <https://doi.org/10.1016/j.polymertesting.2017.04.028>.
- K. Hailu, G. Guthausen, W. Becker, A. König, A. Bendfeld, E. Geissler, In-situ characterization of the cure reaction of HTPB and IPDI by simultaneous NMR and IR measurements, *Polym. Test.* 29 (2010) 513–519, <https://doi.org/10.1016/j.polymertesting.2010.03.001>.
- M.A. Vargas, K. Sachsenheimer, G. Guthausen, *In-situ* investigations of the curing of a polyester resin, *Polym. Test.* 31 (2012) 127–135, <https://doi.org/10.1016/j.polymertesting.2011.10.004>.
- X. Zhang, G.O. Jones, J.L. Hedrick, R.M. Waymouth, Fast and selective ring-opening polymerizations by alkoxides and thioureas, *Nature Chem* 8 (2016) 1047–1053, <https://doi.org/10.1038/nchem.2574>.
- C. Wulf, M. Reckers, A. Perechodjuk, T. Werner, Catalytic systems for the synthesis of biscarbonates and their impact on the sequential preparation of non-isocyanate polyurethanes, *ACS Sustainable Chem. Eng.* 8 (2020) 1651–1658, <https://doi.org/10.1021/acssuschemeng.9b06662>.
- R.M. Garipov, V.A. Sysyov, V.V. Mikheev, A.I. Zagidullin, R.Ya Deberdeev, V. I. Irzhak, AlAl Berlin, Reactivity of cyclocarbonate groups in modified epoxy-amine compositions, *Dokl. Phys. Chem.* 393 (2003) 289–292, <https://doi.org/10.1023/B:DOPC.0000003463.07883.c9>.
- R. Wei, C.L. Dickson, D. Uhrin, G.C. Lloyd-Jones, Rapid estimation of T1 for quantitative NMR, *J. Org. Chem.* 86 (2021) 9023–9029, <https://doi.org/10.1021/acs.joc.1c01007>.
- P.B. Kingsley, Methods of measuring spin-lattice (T1) relaxation times: an annotated bibliography, *Concepts Magn. Reson.* 11 (1999) 243–276, [https://doi.org/10.1002/\(SICI\)1099-0534\(1999\)11:4<243::AID-CMR5>3.0.CO;2-C](https://doi.org/10.1002/(SICI)1099-0534(1999)11:4<243::AID-CMR5>3.0.CO;2-C).
- R. Freeman, H.D.W. Hill, High-resolution studies of nuclear spin-lattice relaxation, *J. Chem. Phys.* 51 (1969) 3140–3141, <https://doi.org/10.1063/1.1672474>.
- R.L. Vold, J.S. Waugh, M.P. Klein, D.E. Phelps, Measurement of spin relaxation in complex systems, *J. Chem. Phys.* 48 (1968) 3831–3832, <https://doi.org/10.1063/1.1669699>.
- V. Salvado, Synthèse et caractérisation de poly(hydroxy-uréthane)s biosourcés dérivés d'érythritol: application à la gélification d'huiles végétales, Université de Bordeaux, France, 2022. PhD thesis, <https://tel.archives-ouvertes.fr/tel-03774084>.
- C. Bakkali-Hassani, D. Berne, P. Bron, L. Irusta, H. Sardon, V. Ladmiraal, S. Caillol, Polyhydroxyurethane covalent adaptable networks: looking for suitable catalysts, *Polym. Chem.* 14 (2023) 3610–3620, <https://doi.org/10.1039/D3PY00579H>.
- J. Xu, X. Wang, J. Liu, X. Feng, Y. Gnanou, N. Hadjichristidis, Ionic H-bonding organocatalysts for the ring-opening polymerization of cyclic esters and cyclic carbonates, *Prog. Polym. Sci.* 125 (2022) 101484, <https://doi.org/10.1016/j.proppolymsci.2021.101484>.

- [46] Y. He, V. Goel, H. Keul, M. Möller, Synthesis, characterization, and selectivity of bifunctional couplers, *Macromol. Chem. Phys.* 211 (2010) 2366–2381, <https://doi.org/10.1002/macp.201000340>.
- [47] B. Ochiai, M. Matsuki, T. Miyagawa, D. Nagai, T. Endo, Kinetic and computational studies on aminolysis of bicyclic carbonates bearing alicyclic structure giving alicyclic hydroxyurethanes, *Tetrahedron* 61 (2005) 1835–1838, <https://doi.org/10.1016/j.tet.2004.12.014>.
- [48] A.Z. Yu, R.A. Setien, J.M. Sahouani, J. Docken, D.C. Webster, Catalyzed non-isocyanate polyurethane (NIPU) coatings from bio-based poly(cyclic carbonates), *J Coat Technol Res* 16 (2019) 41–57, <https://doi.org/10.1007/s11998-018-0135-7>.
- [49] S. Tshepelevitsh, A. Kütt, M. Lökov, I. Kaljurand, J. Saame, A. Heering, P. G. Plieger, R. Vianello, I. Leito, On the basicity of organic bases in different media, *Eur. J. Org Chem.* 2019 (2019) 6735–6748, <https://doi.org/10.1002/ejoc.201900956>.
- [50] A. Bossion, R.H. Aguirresarobe, L. Irusta, D. Taton, H. Cramail, E. Grau, D. Mecerreyes, C. Su, G. Liu, A.J. Müller, H. Sardon, Unexpected synthesis of segmented poly(hydroxyurea–urethane)s from dicyclic carbonates and diamines by organocatalysis, *Macromolecules* 51 (2018) 5556–5566, <https://doi.org/10.1021/acs.macromol.8b00731>.
- [51] B. Lin, R.M. Waymouth, Urea anions: simple, fast, and selective catalysts for ring-opening polymerizations, *J. Am. Chem. Soc.* 139 (2017) 1645–1652, <https://doi.org/10.1021/jacs.6b11864>.
- [52] A. Bossion, K.V. Heifferon, L. Meabe, N. Zivic, D. Taton, J.L. Hedrick, T.E. Long, H. Sardon, Opportunities for organocatalysis in polymer synthesis via step-growth methods, *Prog. Polym. Sci.* 90 (2019) 164–210, <https://doi.org/10.1016/j.progpolymsci.2018.11.003>.
- [53] H. Tomita, F. Sanda, T. Endo, Model reaction for the synthesis of polyhydroxyurethanes from cyclic carbonates with amines: substituent effect on the reactivity and selectivity of ring-opening direction in the reaction of five-membered cyclic carbonates with amine, *J. Polym. Sci. Polym. Chem.* 39 (2001) 3678–3685, <https://doi.org/10.1002/pola.10009>.
- [54] H. Tomita, F. Sanda, T. Endo, Structural analysis of polyhydroxyurethane obtained by polyaddition of bifunctional five-membered cyclic carbonate and diamine based on the model reaction, *J. Polym. Sci. Polym. Chem.* 39 (2001) 851–859, [https://doi.org/10.1002/1099-0518\(20010315\)39:6<851::AID-POLA1058>3.0.CO;2-3](https://doi.org/10.1002/1099-0518(20010315)39:6<851::AID-POLA1058>3.0.CO;2-3).
- [55] A. Steblyanko, W. Choi, F. Sanda, T. Endo, Addition of five-membered cyclic carbonate with amine and its application to polymer synthesis, *J. Polym. Sci., Part A: Polym. Chem.* 38 (2000) 2375–2380, [https://doi.org/10.1002/1099-0518\(20000701\)38:13<2375::AID-POLA100>3.0.CO;2-U](https://doi.org/10.1002/1099-0518(20000701)38:13<2375::AID-POLA100>3.0.CO;2-U).
- [56] D. Gerard, Etude de la réaction Carbamate/Aldéhyde et son application vers de nouveaux matériaux thermodurcissables, Université de Lyon, France, 2020. PhD thesis, <https://tel.archives-ouvertes.fr/tel-03210609>.