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# **Study of the carbamate / aldehyde reaction, a new pathway towards NIPU materials**

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# Study of the carbamate / aldehyde reaction, a new pathway towards NIPU materials

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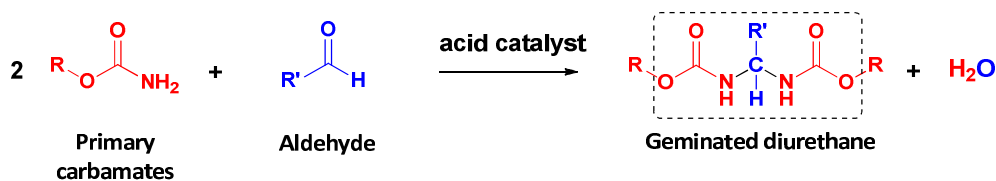
**ABSTRACT** : An innovative alternative to the synthesis of non-isocyanate polyurethanes (NIPUs) thermoset materials was thoroughly investigated. This pathway, involving the reaction between primary carbamate functions and aldehyde functions, was studied using model reactions between ethyl carbamate and different aldehydes that lead to the highlights of the key parameters as well as the first reported proposed mechanism for this reaction. In a second time, polycarbamates synthesized from two different polyols were synthesized via transcarbamoylation before participating in a polycondensation reaction with different monoaldehydes. First a linear NIPU oligomer was synthesized using a dicarbamate derived from ethylene glycol and benzaldehyde. This product was analyzed by NMR spectroscopy and MALDI-TOF mass spectrometry. This oligomer exhibited low molar masses attributed to many secondary termination reactions, mainly due to the presence of acetic anhydride used as solvent in the reaction. Cross-linked NIPU materials were then synthesized without solvent, from the reaction between a tricarbamate derived from trimethylol propane and vanillin, a biobased monoaldehyde, for the first time. The process parameters for the synthesis of these materials were optimized to obtain biobased NIPU thermosetting networks with gel fraction (GF) in dimethylsulfoxide (DMSO) up to 82%, with  $T_g$  values ranging between 39°C and 65°C depending on the GF value. This study brings a much needed highlight on the little-known carbamate / aldehyde reaction and demonstrates its potential for the synthesis of novel biobased NIPU thermosetting coatings using a simple monoaldehyde such as vanillin.

**Keywords** : aldehyde, primary carbamate, non-isocyanate polyurethane (NIPU), geminated urethanes, thermosetting coating, biobased, vanillin

## INTRODUCTION

The vast majority of the crosslinking systems currently involved in the synthesis of thermosetting polymers require the use of hazardous components for the environment as well as for the operators. Polyurethanes (PU), which are among the most important polymer materials thanks to their versatile properties, are not an exception to this issue. Polyurethanes are indeed classically obtained by polyaddition between a polyol and a polyisocyanate, the synthesis of the latter involving the use of highly toxic derivatives such as phosgene [1]. The development of safer and eco-friendlier alternatives to those already existing crosslinking systems are thus of particular interest for both academic and industrial research teams [2,3]. Two synthesis pathways attracted most of the attention these last few years in order to obtain non-isocyanate polyurethane (NIPU): the transurethanization of bis-carbamates and polyols [4-7], and the polyaddition of polyamines and bis- or poly-cyclic carbonates [8-12]. If both ways lead to the formation of PU without the direct use of any isocyanate or phosgene derivatives, they still suffer from many weaknesses. In the first case, processing at high temperatures is required. In the second case, a slow kinetics (particularly for 5-membered ring carbonates) as well as side reactions leading to low molar masses are often encountered [13]. Although recently some of those pitfalls were circumvented by the use of multifunctional precursors lowering the gel conversion [14], or avoided by that of activated carbonates such as  $\alpha$ -alkylidene 5-membered carbonates [15,16] leading to thermally stable unsaturated polyoxazolidones, the problem remains when considering the synthesis of standard  $\beta$ -hydroxy urethane bonds. This explains why these synthetic routes are still limited to academic researches despite an outstanding applicative potential [17].

The present work aims to study an alternative pathway to making novel NIPU materials using the carbamate / aldehyde (CA) reaction. This reaction is operated in acidic conditions and implies two carbamate functions for each aldehyde group, thus forming a double urethane function on a single carbon that will be called a geminated diurethane function in this paper (**FIGURE 1**). It is important to note that only primary carbamates can be involved in this reaction. Moreover, this reaction would be particularly well suited to the preparation of innovative and potentially biobased organic coatings, or even foams, since it generates water.



**FIGURE 1** Geminated diurethane synthesis from the reaction between primary carbamates and an aldehyde under acidic conditions.

Although being known since the 19<sup>th</sup> century with the works of D. Roth in 1870 [18], this reaction has not been extensively studied even to this day, providing very little information about the reaction's key parameters or mechanism. However, quite recently, it received more attention as polycarbamate / polyaldehyde cross-linking has been reported to make NIPU coatings [3,19-21]. Indeed, it possesses many advantages that make it suitable and interesting to obtain thermosetting PU resins, such as versatility and possibility to cure at ambient temperature with a simple acid catalyst. However, a significant limitation lies in the lack of readily available polyaldehydes. In fact, publications on this cross-linking systems are often limited to a mixture of 1,3- and 1,4-cyclohexanedicarboxaldehyde (CHDA), a petro-derived dialdehyde [3,19,20]. Silbert *et al.* proposed the diformylfuran (DFF) as a bio-derived alternative to CHDA, but until recently the market availability and price of this product was still an issue [21]. In fact, most of the authors using DFF as the precursor of new polymer materials synthesized this reactant by themselves [21,22].

In this paper, we propose an in-depth study of the CA reaction using model compounds that allowed us to establish a mechanism highlighting the key parameters of this pathway. Thereafter, the synthesis of new NIPU linear oligomers and networks was explored using monoaldehydes, much more available than their difunctional homologues. Moreover, in addition to petro-based monoaldehydes, bio-based monoaldehydes were also studied in this system, and especially vanillin considered as a promising biobased building-block in polymer chemistry [23]. Two main processes were explored: the first is operated at low temperature (<80°C) in presence of acetic anhydride that, as shown below does not only act as a solvent (**process A**) but also takes part in the reaction by scavenging water, also leading to undesired side products. The second one is operated in bulk at higher temperature (>100°C) (**process B**). The obtained NIPU oligomers and networks were then characterized and the results were discussed in the lights of the observations highlighted in the mechanistic study.

## EXPERIMENTAL SECTION

### Chemicals

All chemicals were used as received. Products for model reactions are: ethyl carbamate, benzaldehyde, vanillin, 5-methyl furfural (5-MF), cyclohexane carboxaldehyde (CC), n-heptanaldehyde, trifluoroacetic acid (TFA), ethylphosphonic acid (EPA), acetic acid, and acetic anhydride, all purchased from Sigma-Aldrich. For the synthesis of NIPU linear oligomers and networks, polycarbamates were synthesised directly using ethylene glycol, trimethylolpropane (TMP) methyl carbamate and dibutyltin oxide (DBTO), all obtained from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) from Sigma-Aldrich was used in synthesis as well as in analysis, and especially for NMR spectroscopy using its deuterated form (DMSO-

d6) purchased from Euriso-Top. This list, completed with molecular structures and CAS numbers, is presented in the supporting information (SI).

### **Analytical Methods**

NMR spectra were recorded at room temperature on a Bruker Avance spectrometer at 400.13 MHz for  $^1\text{H}$  and 100.61 MHz for  $^{13}\text{C}$  with a 5 mm BBFO1 probe at 300K and processed with Bruker Topspin 3.2 software. 2D analyses were also recorded using this spectrometer, especially  $^1\text{H}$ - $^1\text{H}$  homonuclear correlation spectroscopy (COSY) and  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear spectroscopy (HSQC and HMBC).

Thermal properties were obtained with a DSC Q22 (TA Instruments). Aluminum hermetic capsules were used, and samples of about 5 mg were weighed. Samples were heated from  $-80^\circ\text{C}$  to  $180^\circ\text{C}$ , at a rate of  $10^\circ\text{C}/\text{min}$ .

Thermogravimetric analyses were performed with a Q500 equipment (TA Instruments). Samples were weighed in an aluminum pan, then placed in an oven heated at a fixed isotherm ( $100^\circ\text{C}$ ,  $110^\circ\text{C}$  or  $120^\circ\text{C}$ ). A nitrogen or air flow ( $90\text{ mL}/\text{min}$ ) was introduced into the oven to study the role of oxidation on the samples.

The MALDI-TOF mass spectrometry analysis was performed with a Voyager-DE PRO (Applied Biosystems, Framingham, MA) equipped with a nitrogen laser emitting at 337 nm with a 3-ns pulse duration. The instrument was operated in linear and reflectron modes. Samples were prepared by mixing them in a CHCA ( $\alpha$ -Cyano-4-Hydroxycinnamic Acid) matrix with a sodium salt to enhance cationization, using DMSO as co-solvent. The resulting mixtures were spotted on the MALDI sample plate and air-dried before analysis.

Gel fractions (GF) of NIPU networks were assessed by inserting a known mass  $m_i$  of the recovered material in a known volume of DMSO, a good solvent of the monomers and PU oligomers. After 2h at  $25^\circ\text{C}$ , the sample was filtered, washed with DMSO and acetone before drying and weighing ( $m_f$ ). The gel fraction was then given by  $\text{GF} = m_f/m_i$ . The aim is to obtain a fully insoluble material ( $\text{GF} = 100\%$ ) in order to prove the complete reticulation of the network.

### **Typical procedure for the model reaction synthesis**

The procedure used to study the CA reaction was inspired by the literature [24]. A typical synthesis was as follows: benzaldehyde (2.4 g, 1 eq) and ethyl carbamate (4 g, 2 eq) were introduced in a round-bottom flask with 8 mL (3.8 eq) of acetic anhydride and stirred at room temperature until complete homogenisation. Trifluoroacetic acid, TFA was then added (0.27 g, 0.1 eq), marking the start of the reaction. In each case, a white precipitate was observed after only few minutes of reaction and therefore the reaction was stopped after 1 hour, more than enough to complete the reaction. The

precipitate was then filtered and washed by acetic anhydride, then dried in an oven at 40°C before characterization. Finally,  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses were performed to confirm the geminated diurethane structure of the product.

### **Typical procedure for the synthesis of polycarbamate precursors from polyol by transurethanization reaction**

In all cases for the subsequent synthesis, polycarbonates were synthesized as a first step from polyols which underwent a transcarbamylation (or transurethanization) reaction with methyl carbamate in presence of DBTO as described in the literature [3,19,20]. Ethylene glycol was used in the case of the difunctional carbamate leading to linear NIPU oligomers while TMP was used as a precursor of the trifunctional carbamate to obtain NIPU networks.

The polyol, being either ethylene glycol or TMP, (40 mmol) and methyl carbamate (320 - 400 mmol) were introduced in a two-neck round-bottom flask and heated at 120°C under magnetic stirring. Upon complete fusion of the methyl carbamate, the catalyst (DBTO, 2 mmol) was then added, and the formed mixture was stirred at 120°C under a constant nitrogen flow until completion of the reaction (18-24h), as indicated by the NMR spectra of the reaction mixture (SI, Figures S1-S3). Finally, the crude product was washed by acetone and dried before being analysed and used in further synthesis.

Methyl carbamate was used in excess because of its tendency to sublime during the reaction, which can impact the stoichiometry if not taken into account. In order to lessen the impact of this phenomenon, the flask was equipped with a water column, with the temperature of water flowing through it fixed at 60°C. This device allowed most of the methyl carbamate vapours to condense in the column and thus fall back into the reaction medium.

### **Typical procedure for the synthesis of NIPU linear oligomers and networks**

The previously obtained polycarbonates were further used in two different processes.

#### *Synthesis of linear oligomers*

The first one (**process A**) is a direct application of the aforementioned model reaction synthesis process and was only used for the synthesis of linear NIPU oligomers. A typical synthesis for **A** is as follows: benzaldehyde (0.17 g, 1 eq) and ethylene dicarbamate (0.25 g, 1 eq), obtained from ethylene glycol, were introduced in a round-bottom flask with 0.6 mL (3.8 eq) of acetic anhydride and stirred at 80°C until complete homogenisation. TFA was then added (0.02 g, 0.1 eq), marking the start of the reaction. The reaction was then continued for 15 h before washing the product with the reaction solvent acetic

anhydride (to remove unreacted monomers) and filtration. The product underwent NMR analysis in order to validate its chemical structure.

#### *Synthesis of NIPU networks*

A second process (**process B**) was carried out in bulk and allowed to obtain NIPU networks. In a typical procedure, the tricarbamate (0.5 g, 1 eq), obtained from TMP, and vanillin (0.43 g, 1.5 eq) were mixed in a ceramic cup. This step can be helped by heating the premix above the melting temperature of the aldehyde (81.5°C). EPA (0.02-0.08 g, 0.1-0.4 eq) was then added and mixed with the blend to start the reaction. The obtained premix was then placed in an oven where the temperature and atmosphere of the curing step can be adjusted. After 24 h of curing, the resulting material was cooled at room temperature before characterization, and especially determination of the GF.

## RESULTS AND DISCUSSION

### Model reactions using monofunctional compounds

In order to understand the fundamental characteristics and key parameters of the reaction, model reactions between an aldehyde and ethyl carbamate were first studied. Inspired by a simple experimental procedure of the literature that seemed to lead to good yields with rather similar precursors, acetic anhydride was chosen as solvent [24]. Investigations were more particularly focused on three main parameters: the nature of the aldehyde's substituent used in the reaction, the nature and influence of the acid catalyst, and the role of acetic anhydride in the synthesis. All model reactions were performed in the same conditions: 1 h at room temperature, and a yield was calculated by weighing the washed product and comparing it to the theoretical mass, as presented in Table 1.

**TABLE 1** Model reactions between ethyl carbamate (2 eq) and different aldehydes after 1 h at 25°C

Entry	Aldehyde (1 eq)	Acid catalyst (0.1 eq)	Acetic anhydride (eq)	Yield (%)
1	Benzaldehyde	TFA	3.8	69
2	5-Methyl furfural	TFA	3.8	41
3	Cyclohexane carboxaldehyde	TFA	3.8	66
4	Heptanaldehyde	TFA	3.8	64
5	Vanillin	TFA	3.8	82
6	Benzaldehyde	none	3.8	0
7	Benzaldehyde	Acetic acid	3.8	31
8	5-Methyl furfural	EPA	3.8	43
9	5-Methyl furfural	TFA	0	26



The reaction between benzaldehyde and ethyl carbamate was first operated in order to validate this reaction (Table 1, entry 1) and a yield of 69 % was obtained in accordance with the literature [24]. Subsequent trials made clear that this reaction can be extended to various aldehydes, aromatic as well as linear aliphatic (Table 1, entries 2-5) with the same efficiency. Moreover, three of these aldehydes are potentially biobased (5-methyl furfural, heptanaldehyde and vanillin), showing that at least partially biobased PU can be obtained through this pathway. During the reaction, and as shown in Figure 1, water is formed and can subsequently react with the acetic anhydride used as a solvent but that obviously also plays the role of desiccant. Acetic acid is then formed *in situ*, both from ambient humidity and from the reaction with water.

The question was then: is it possible to use only this created acetic acid as the required acid catalyst? After 1 h when no acid catalyst was used (Table 1, entry 6), no reaction was observed, showing that the *in situ* formation of acetic acid from acetic anhydride is not enough to catalyse the reaction. Moreover, it was observed that the catalytic activity of acetic acid was weaker than that of TFA in the same conditions (Table 1, entry 7). This presumably results from the difference of pKa of the two acids ( $pK_{a(\text{acetic acid})} = 4.7$  whereas  $pK_{a(\text{TFA})} = 0.3$ ). In order to replace TFA with a safer acid catalyst, different other organic acids were tested that would offer better alternatives than metal catalysts both for health and environment. Indeed, metallic catalysts are often hazardous and difficult to eliminate in the final product, which is why organic catalysts are seen more and more as the preferable alternative [25]. In this case, we chose to use phosphonic acids, since they have already shown a good activity for PU synthesis [26]. And with our system, ethylphosphonic acid, EPA was a good candidate : it gives similar results as TFA under the same conditions (Table 1, entry 8) but, although displaying a rather comparable toxicity, it has a significantly lower impact on the environment (no hazard statement relative to environment whereas TFA is classified H412 "Harmful to aquatic life with long lasting effects"). Finally, the reaction was operated in bulk (Table 1, entry 9), and a negative impact on the reaction from the absence of acetic anhydride could be noted, which shows that this compound does not only act as a solvent. We hypothesized that acetic anhydride also acts as a hygroscopic agent, consuming the water formed during the reaction and thus shifting the equilibrium of the reaction towards the product.

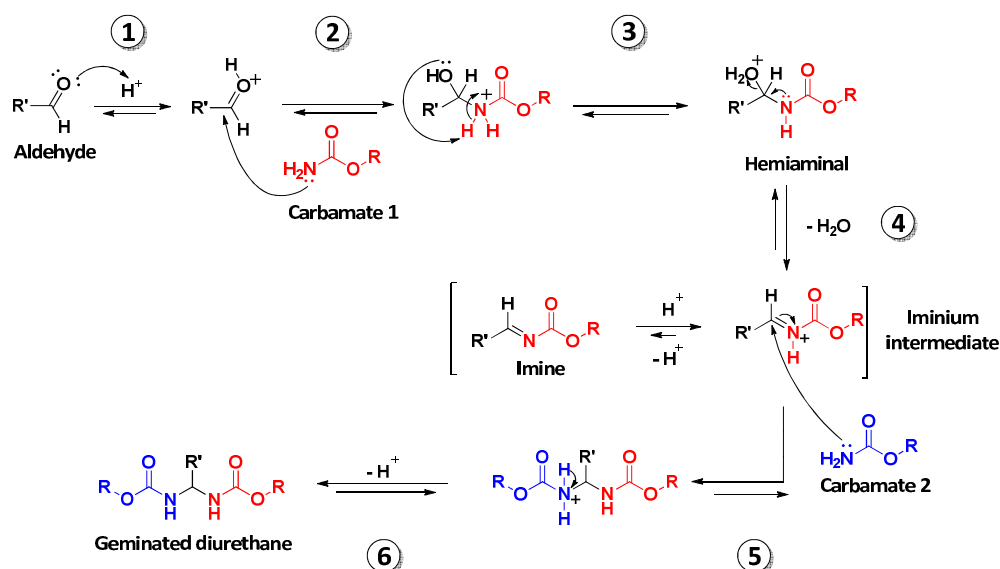
### Mechanistic study of the CA reaction

From the previous experimental data, a tentative mechanism of reaction was proposed and further validated, as presented in **FIGURE 2**.

This mechanism is divided into 6 steps that can be detailed as follows:

- ① Activation of the carbonyl by the acidic proton from the catalyst.

- ② Nucleophilic attack of the carbonyl by the nitrogen atom of a first carbamate group.
- ③ Structural rearrangement in order to obtain a hemiaminal structure
- ④ Release of a water molecule and formation of an intermediate in the form of an iminium ion that can stabilize itself directly in its imine form. However, even when fostering the monosubstitution by an excess of aldehyde, the imine form was never observed in our model monofunctional reactions. Indeed, this imine might not be stable if the released water is not properly eliminated from the medium.
- ⑤ Stabilization of the iminium intermediate by the nucleophilic attack of a second carbamate group.
- ⑥ Release of an acidic proton in order to obtain the geminated diurethane structure and thus closing the catalytic cycle of the reaction.



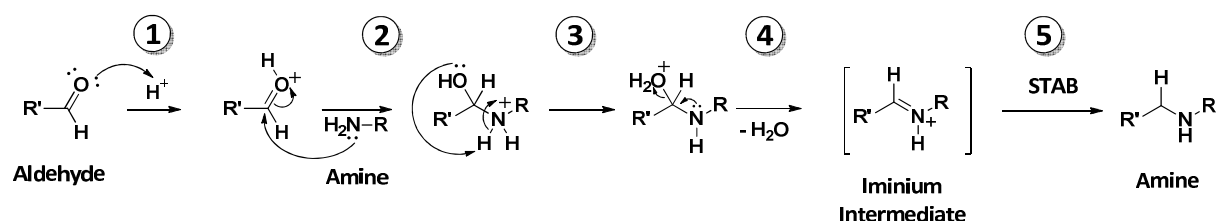
**FIGURE 2** Proposed mechanism for the carbamate / aldehyde reaction

Moreover, in order to improve the conversion of the reaction the necessity to eliminate water from the reaction medium as soon as it is formed was already pointed out. This translates to the existence of equilibria in the steps ① through ④. Likewise, the last two steps can be considered as equilibria; this would be consistent with the acidic hydrolysis observed in the past under appropriate conditions (i.e. by boiling for a short time with normal aqueous hydrochloric acid) for the geminated diurethane compounds and leading back to the original reactants [27].

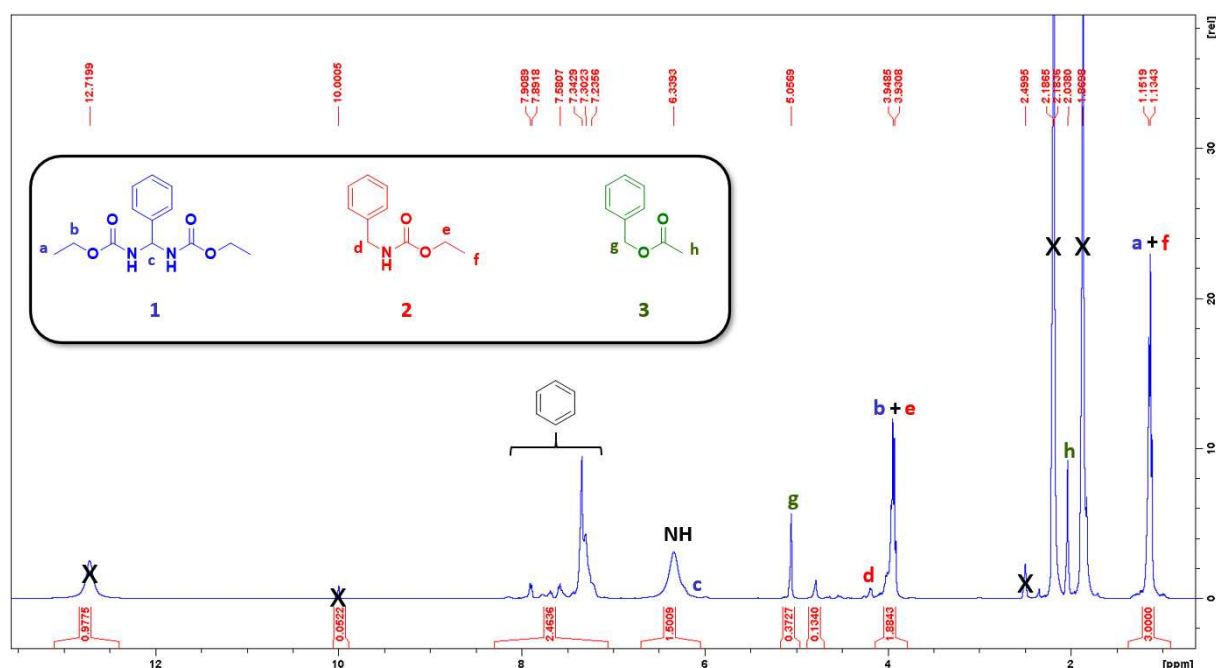
#### Evidences of the iminium intermediate's existence

In order to validate this mechanism, the existence of the proposed iminium intermediate needs to be proved. It was first attempted to observe directly the intermediate *in situ* using FTIR-ATR monitoring of the CA reaction at 100°C for 2 hours (SI, Figure S4). However, this analysis was not convincing enough

to prove the existence of this iminium intermediate, therefore a second method was used to observe it, indirectly this time. Indeed, when looking at the mechanism of the reductive amination of aldehydes in **FIGURE 3**, it appears that the four first steps of this reaction are identical to those of the proposed mechanism (with  $R = \text{COOR}^1$ ). The idea was then to add a reducing agent such as STAB (Sodium Triacetoxyborohydride) in the model CA reaction between ethylcarbamate and benzaldehyde (Table 1, entry 1). The raw product of this reaction was then analysed by complete NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, HSQC and HMBC) in order to identify the different structures obtained thereof. The obtained spectra are displayed in **FIGURE 4** and in SI (Figures S5-S9).



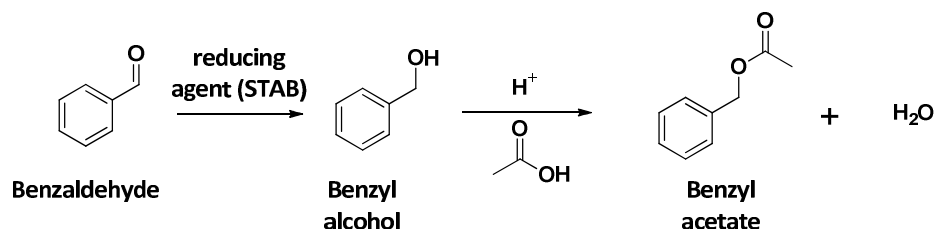
**FIGURE 3** Reaction mechanism of the reductive amination of aldehydes [28]



**FIGURE 4**  $^1\text{H}$  NMR spectrum in  $\text{DMSO}-d_6$  at room temperature of the raw products of the CA reaction between ethylcarbamate and benzaldehyde in presence of STAB. Crossed signals are due to the presence of acetic anhydride and acetic acid in the raw sample.

The  $^1\text{H}$  NMR spectrum displayed in **FIGURE 4** shows that 3 different structures can be identified: a geminated diurethane structure (**1**) from the CA reaction between ethylcarbamate and benzaldehyde (whose presence is confirmed by the small “c” signal at 6.05 ppm); a monourethane structure (**2**) from the reductive amination of benzaldehyde by ethylcarbamate and STAB; and finally, benzyl acetate as the majority structure (**3**). The  $^1\text{H}$  NMR spectra of structures **2** and **3** (respectively ethyl N-benzyl

carbamate [2621-78-5] for product **2**, and benzyl acetate [140-11-4] for compound **3**) can be found in several literature databases and confirm the presence of those 2 compounds. Structure **3**, although unwanted, can be explained by a reaction between benzyl alcohol and acetic acid in acidic conditions, which explains its high proportion since acetic anhydride, giving acetic acid directly through hydrolysis, is the solvent of the reaction. Benzyl alcohol comes directly from the reduction of benzaldehyde by a reducing agent such as STAB (**FIGURE 5**).



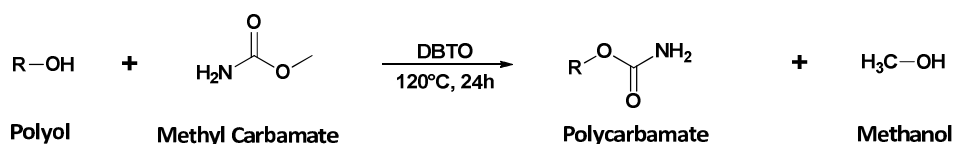
**FIGURE 5** Origin of the observed benzyl acetate from benzaldehyde in presence of a reducing agent (STAB)

However, an important result is the concomitant presence of both the structures **1** and **2** that means that there was a competition between the CA reaction and the reductive amination, hence our conclusion that both reactions imply the same iminium intermediate.

As a conclusion to this part, we first tried to observe directly the hypothesized iminium intermediate for the CA reaction by FTIR-ATR analysis. However, the results were not conclusive enough to validate the existence of such an intermediate. We then showed that the CA reaction indeed seems to pass through an iminium intermediate by stabilizing it in another form using the reductive amination reaction.

### Polycarbamate synthesis from the transcarbamylation reaction of polyols

The first step towards the synthesis of PU using CA reaction is the synthesis of polycarbamate precursors. These precursors are obtained from the transcarbamylation reaction of polyols with methyl carbamate (**FIGURE 6**).



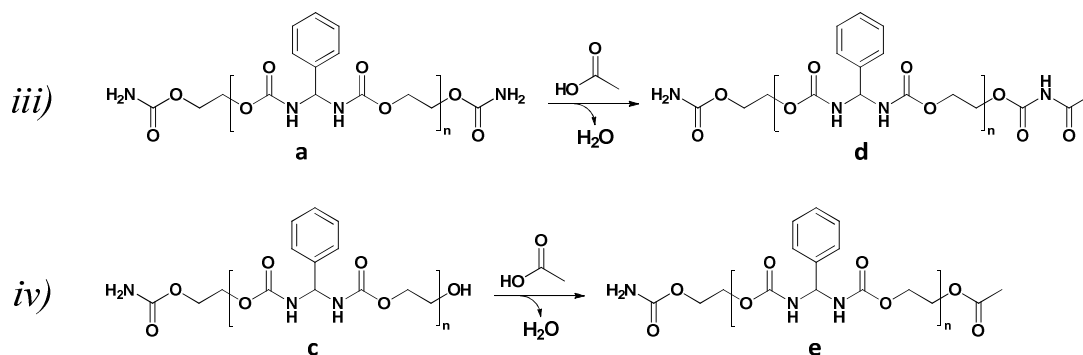
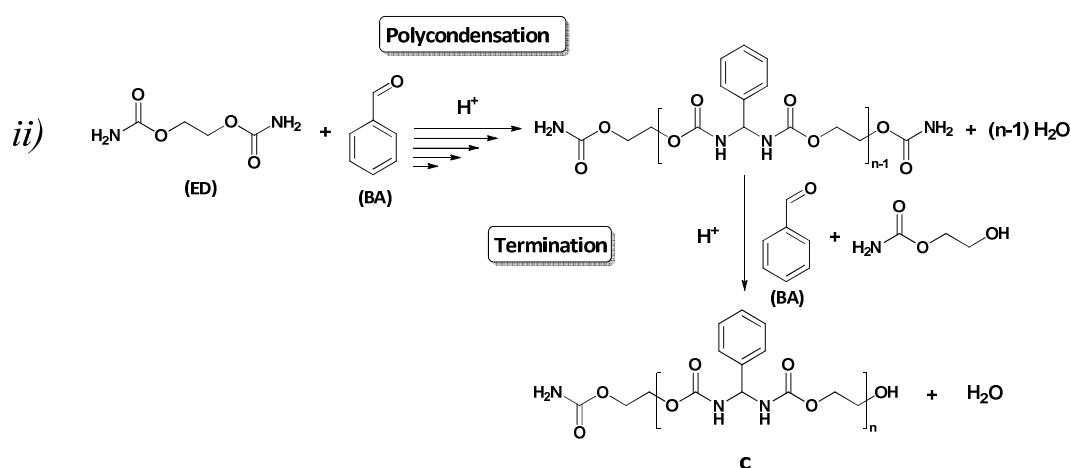
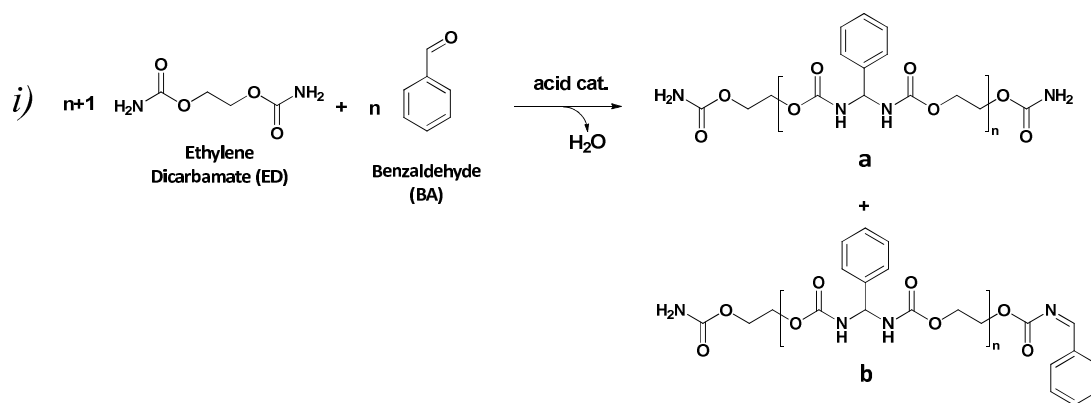
**FIGURE 6** Synthesis of a polycarbamate from a polyol and methyl carbamate through transcarbamylation reaction

Two polyols were used depending on the functionality wanted on the final polycarbamate precursor: ethylene glycol for the synthesis of a dicarbamate, and TMP for the synthesis of a tricarbamate. After purification, the yield was 35-45% for the dicarbamate, and 60-70% for the tricarbamate, with the best

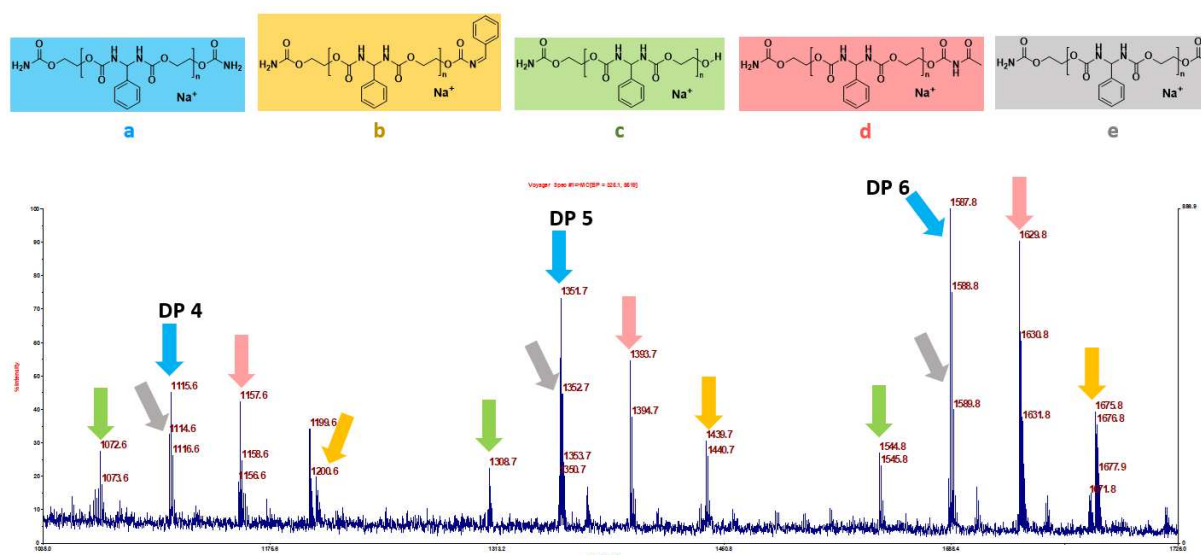
yields corresponding to larger excesses of methyl carbamate. In both cases, the washed product was analyzed by NMR spectroscopy showing a satisfactory purity for subsequent CA reactions. However, the  $^1\text{H}$  NMR spectra displayed in the SI (Figures S1,S3) show that traces of excess methyl carbamate can remain in the final polycarbamate. Likewise, some alcohol functions from the original polyol can remain on the polycarbamate chain, even if these traces are not observed on the NMR spectra. These residual traces can be the cause of unwanted secondary reactions, as observed later in this paper.

### **Linear polymerization through CA reaction**

Using **process A**, a NIPU oligomer was synthesized from ethylene dicarbamate and benzaldehyde, using acetic anhydride as solvent and TFA as acid catalyst (**FIGURE 7 i)**). The obtained oligomer was then analysed by NMR spectroscopy as well as mass spectroscopy (MALDI-TOF). Using this last technique, molar masses up to  $3760 \text{ g.mol}^{-1}$  (DP=15) with a very broad distribution were detected (SI, Figure S10). SEC analysis was unable to confirm these results due to insolubility issues of the oligomer in all tested possible eluents. However, mass spectroscopy analysis was especially useful to identify the different structures in our sample, explaining the broad distribution and low molar masses (**FIGURES 7 and 8**).



**FIGURE 7** Synthesis of a NIPU linear oligomer from ethylene dicarbamate and benzaldehyde, showing secondary reactions leading to alternative structures identified in the sample



**FIGURE 8** MALDI-TOF mass spectrum of the NIPU oligomers obtained from ethylene dicarbamate and benzaldehyde. All identified structures are highlighted.

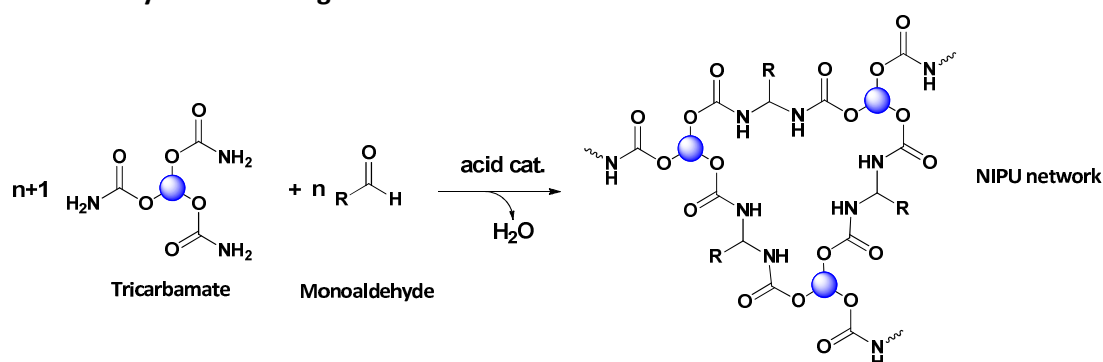
The first structure (**a**) is in majority, and has been identified as the expected product of the CA reaction between ethylene dicarbamate and benzaldehyde (**FIGURE 7 i**). Structure **b** presents one imine group as chain end, which can be due to the direct stabilization of the iminium intermediate during the CA reaction (**FIGURE 7 i**). Although this imine group was not observed in the monofunctional model reactions, our hypothesis is that this structure becomes more stable as the chains grow. Structure **c** presents an alcohol function that terminated the reaction (**FIGURE 7 ii**). This alcohol function may originate from residual alcohol functions in the ethylene dicarbamate used for the synthesis, as noted previously. Finally, both structures **d** and **e** come from a secondary reaction involving acetic anhydride and terminating the reaction (**FIGURE 7 iii** and **iv**). One can assume that the low molar masses obtained for the studied oligomers are directly linked to the many different secondary end-capping reactions brought into play, especially due to the presence of acetic anhydride that behaves as a chain stopper. This justifies why it was decided to rule out acetic anhydride in the next step.

Several attempts of linear polymerization were at first made in the presence of TFA, using DMSO as solvent and replacing acetic anhydride with other water scavengers such as anhydrous magnesium sulfate, ethyl orthoformate or even molecular sieves (3 Å); however for all those trials no reaction was observed, neither at 25 nor at 80°C.

Another attempt was then made in DMSO at 100°C, without acetic anhydride nor any other desiccant, and after 24 h led to a yield ~ 52%, without the side products ascribed to acetic anhydride (see SI, Figure S11). The full chemical characterization of this product was impeded by its poor solubility, except for the shortest oligomers, but this process could be a suitable way of preparing satisfactory thin coatings by CA reaction.

In order to prepare thick, solid materials, it was finally decided to use a different process (**process B**), which also allowed to successfully eliminate most secondary reactions.

### NIPU network synthesis through CA reaction



**FIGURE 9** General synthesis of a NIPU network from a tricarbamate and a monoaldehyde

To the best of our knowledge, only two other teams developed NIPU networks using CA reaction [3,21], and in each case, dialdehydes were used in order to obtain the materials. However, since each aldehyde function has a functionality of 2 in the CA reaction, reacting a monoaldehyde with a polycarbamate with a functionality strictly higher than 2 in stoichiometric proportions is enough to obtain a cross-linked material (**FIGURE 9**) [29]. In this paper, we report the formation of a NIPU network by reacting a tricarbamate obtained from TMP with a biobased monoaldehyde: vanillin.

In those preliminary trials only aiming at a first overview of the material aspect, we chose not to use a solvent (e.g. DMSO) that would probably allow the preparation of bubble-free samples with well-defined geometries. Therefore a bulk process (**process B**) was used to avoid using acetic anhydride that causes secondary reactions, and the used curing temperatures were above 100°C in order to eliminate most of the water formed during the reaction. However, rather thick samples (several millimetres) with numerous remaining bubbles were obtained. EPA has been chosen as the acid catalyst since it was the most adapted to the process conditions (mp = 61°C and low volatility). The temperature and atmosphere of the oven used for the 24h curing step were both adjustable parameters, as presented in the Table 2.

**TABLE 2** NIPU networks synthesis between vanillin (1.5 eq) and the tricarbamate from TMP (1 eq)

Entry	Acid catalyst (EPA)	Temperature (°C)	Curing atmosphere	Gel fraction (%)	T <sub>g</sub> (°C)
1	0.1 eq	100°C	Air	2	-
2	0.2 eq	100°C	Air	8	-
3	0.4 eq	100°C	Air	9	39°C
4	0.4 eq	110°C	Air	33	-
5	0.4 eq	120°C	Air	63	-
6	0.4 eq	100°C	Argon	57	-
7	0.4 eq	110°C	Argon	61	-
8	0.4 eq	120°C	Argon	82	65°C



The obtained NIPUs were found insoluble in all tested organic polar solvents (tetrahydrofuran, N,N-dimethyl formamide, N,N-dimethylacetamide and dimethyl sulfoxide, DMSO that was subsequently used to determine the gel fractions). The aim of the trials in Table 2 was to identify the important parameters in order to obtain the NIPU material with the most important gel fraction (GF) as possible. Indeed, the first trial (Table 2, entry 1) led to a mere 2 % GF, far from the 100 % needed to validate the completion of the reaction. First, we investigated the impact of the proportion of acid catalyst used on the GF, but even when multiplying it by 4, the GF never exceeded 9 % (Table 2, entries 2 and 3).

The next investigated parameter was the temperature of the curing step and a significant raise of the GF could be observed, from 9 % at 100°C to 63 % at 120°C (Table 2, entry 3 to 5). However, raising the temperature of the curing step does not only affect the reaction rate, but also promotes the thermal degradation of primary carbamate functions. Indeed, a thermal degradation of polycarbamate molecules can be observed that accelerates with the temperature, with a mass loss of ~ 1 wt% per hour at 100°C, up to 6 wt% per hours at 120°C, both in air (SI, Figure S12). This explains the rather low GF obtained even at 120°C because this thermal degradation of primary carbamate functions competing with the CA reaction has a direct impact on its stoichiometry, hence limiting the maximum theoretical conversion.

However, it was observed that this thermal degradation could be reduced by half at 120°C by simply changing the atmosphere for an inert gas such as argon (SI, Figure S13). This can be explained by the fact that primary carbamate functions are particularly sensitive to thermooxidation, as illustrated by the release of CO<sub>2</sub> and derivatives of cyanic acid or short isocyanate molecules suggested by ATG/FTIR coupling analysis (SI, Figure S14) in agreement with literature [30]. Indeed, using an argon atmosphere during the curing step of the CA reaction allowed to lessen the degradation's impact on the stoichiometry, thus significantly increasing the GF, regardless of the temperature, up to 82 % at 120°C (Table 2, entries 6 to 8). Moreover, the increase in the T<sub>g</sub> value of the material with the GF, from 39°C at 9 % GF up to 65°C at 82 % GF confirms the increase in the cross-linking degree of the system. Both DSC thermograms are given in the SI (Figures S15, S16). It can be noted that in both cases, the signal deteriorates, showing the degradation of the sample at high temperature. Moreover, those curves are difficult to exploit as they show many erratic fluctuations.

We could not obtain materials with a GF of 100 %, however such materials should presumably be obtained by finding the appropriate trade-off between reactivity and thermal degradation. For example other polycarbamates with a different chemical structure could be easier to mix with the used aldehydes, and might also display a higher thermal stability that would allow a broader temperature range for processing.

## CONCLUSION

The comprehensive study of the carbamate / aldehyde reaction developed in this paper allowed to propose a mechanism for the first time, in accordance with all experimental observations. The suspected intervention of an iminium intermediate could be indirectly confirmed by the use of a reducing agent. Moreover, extensive NMR analysis also supports the reaction intermediate proposed in our mechanism.

Following the literature, in the preliminary studies involving low-functionality precursors (synthesis of model geminated diurethane and linear polymers), acetic anhydride was successfully used, both as solvent and water scavenger for the CA reaction; however, it turned out that it could also play the role of chain stopper and therefore limit the molar masses. It was then ruled out for the preparation of new materials.

As a follow up, NIPU oligomers and networks were synthesized, and we report for the first time the preparation of NIPU materials using vanillin through CA reaction. These materials present a gel fraction up to 82 % because of the trade-off between reactivity and thermal degradation during the curing step that disturbs the reaction stoichiometry. Although a few improvements are still needed, this work can be used as a bedrock for future investigations on the synthesis of new NIPU coatings based on CA reaction, and especially on using different polycarbamates in order to adjust the material's final properties. The use of a suitable solvent that could allow the preparation of thin, bubble-free coatings with optimized curing would also provide valuable additional characterizations of those new materials. Finally, this reaction implies the formation of water molecules, sometimes in the form of bubbles that should be totally evacuated for coatings; but one could also take advantage of their presence to generate innovative foams, i.e. by adding appropriate surfactants to those formulations.

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## Supporting Information:

### Study of the carbamate / aldehyde reaction, a new pathway towards NIPU materials

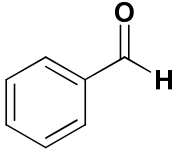
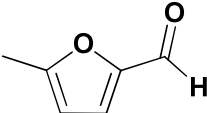
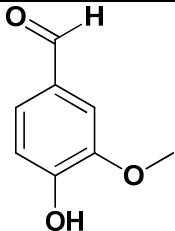
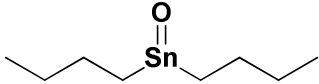
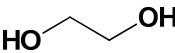
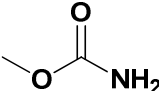
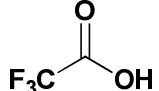
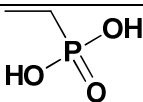
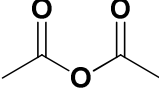
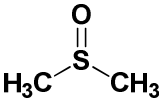
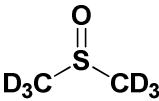
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1. **List of all used chemicals**
2. **Synthesis of polycarbamates from polyols**
  - <sup>1</sup>H NMR spectrum in DMSO-d6 of the purified product
  - <sup>13</sup>C NMR spectrum in DMSO-d6 of the purified product
  - <sup>1</sup>H NMR spectrum in DMSO-d6 of the purified product
3. **FTIR-ATR kinetic analysis for the direct observation of the suspected iminium intermediate**
4. **Evidences of the presence of iminium intermediate's existence: complete NMR spectra of the reaction's raw product**
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  - COSY spectrum
  - HSQC spectrum
  - HMBC spectrum
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6. **Comparison between compounds synthesized with or without acetic anhydride**
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  - TGA thermogram of methyl dicarbamate at a 120°C isotherm in air and inert atmosphere
  - TGA / FTIR coupling analysis of methyl dicarbamate in air, showing the TGA thermogram as well as its derivated curve
8. **Thermal properties of NIPU networks**
  - DSC thermogram of NIPU network 1 (IP = 9 %)
  - DSC thermogram of NIPU network 8 (IP = 82 %)

## 1. List of all used chemicals

Name	Chemical structure	CAS	Provider
Benzaldehyde		100-52-7	Sigma-Aldrich
5-Methyl Furfural		620-02-0	Sigma-Aldrich
Vanillin		121-33-5	Sigma-Aldrich
Dibutyltin Oxide (DBTO)		818-08-6	Sigma-Aldrich
Ethylene glycol		107-21-1	Sigma-Aldrich
Methyl carbamate		598-55-0	Sigma-Aldrich
Trifluoroacetic acid (TFA)		76-05-1	Sigma-Aldrich
Ethylphosphonic acid (EPA)		6779-09-5	Sigma-Aldrich
Acetic anhydride		108-24-7	Sigma-Aldrich
Dimethylsulfoxide (DMSO)		67-68-5	Sigma-Aldrich
Deuterated Dimethylsulfoxide (DMSO- <i>d</i> 6)		2206-27-1	Euriso-Top

## 2. Synthesis of polycarbamates from polyols

Ethylene Dicarbamate was synthesized using ethylene glycol as the polyol.

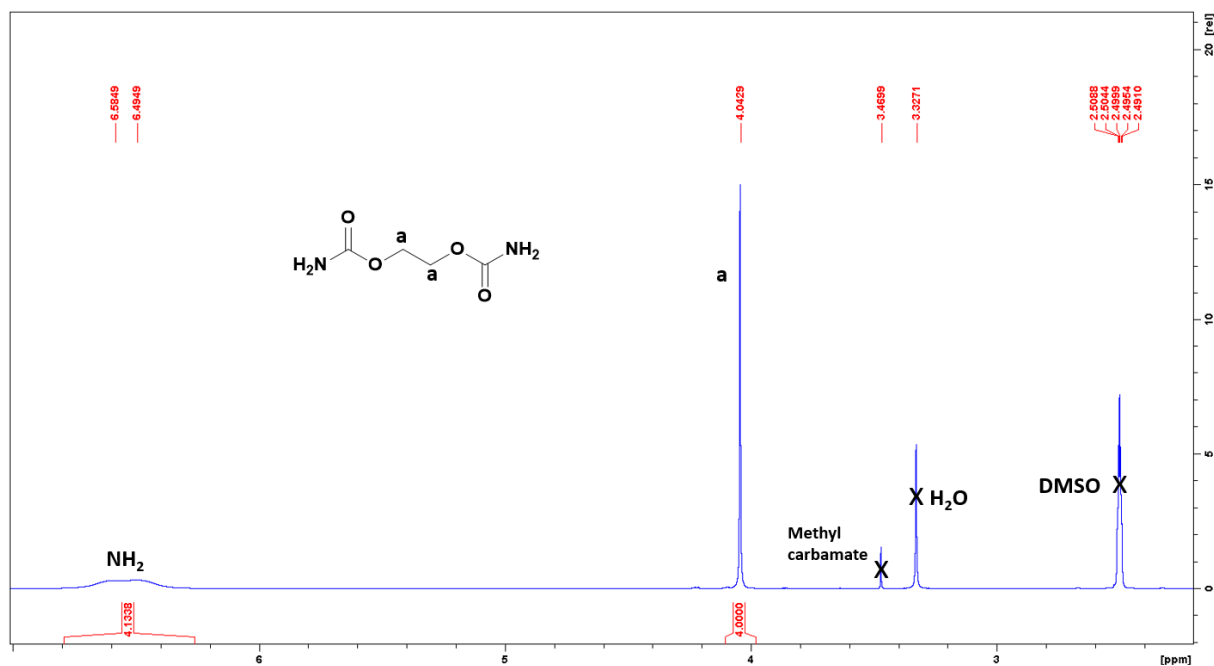


Figure S1 :  $^1\text{H}$  NMR spectrum in  $\text{DMSO-d}_6$  of the purified product

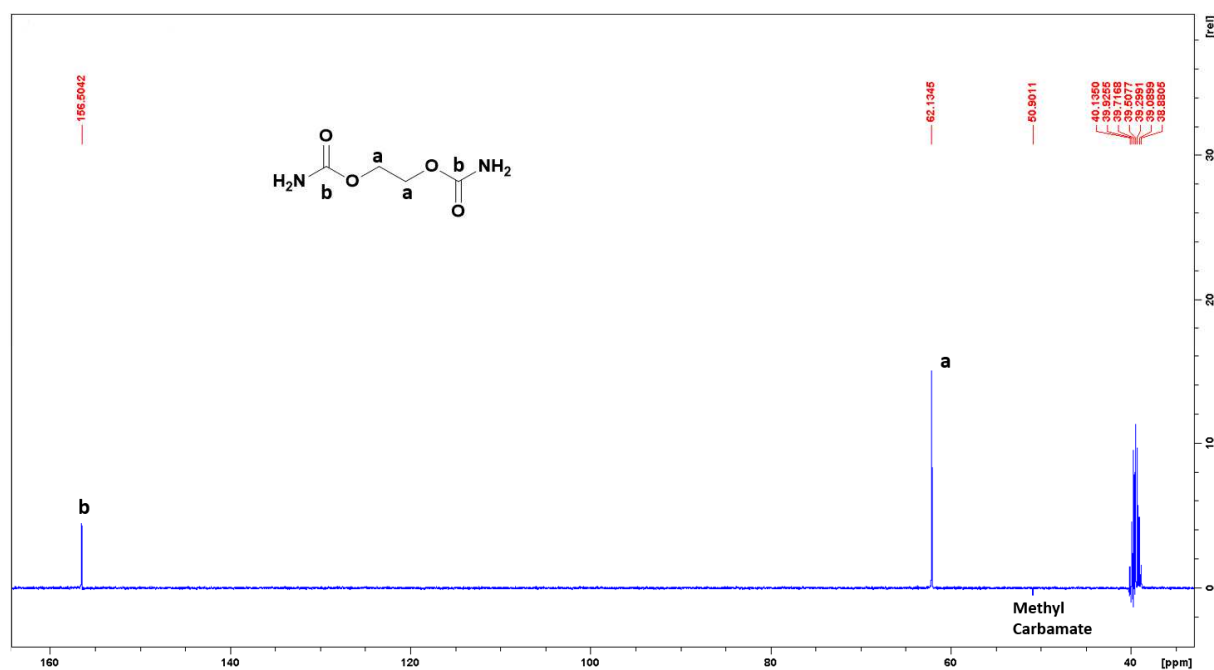


Figure S2 :  $^{13}\text{C}$  NMR spectrum in  $\text{DMSO-d}_6$  of the purified product



A tricarbamate was synthesized using trimethylol propane (TMP) as the polyol.

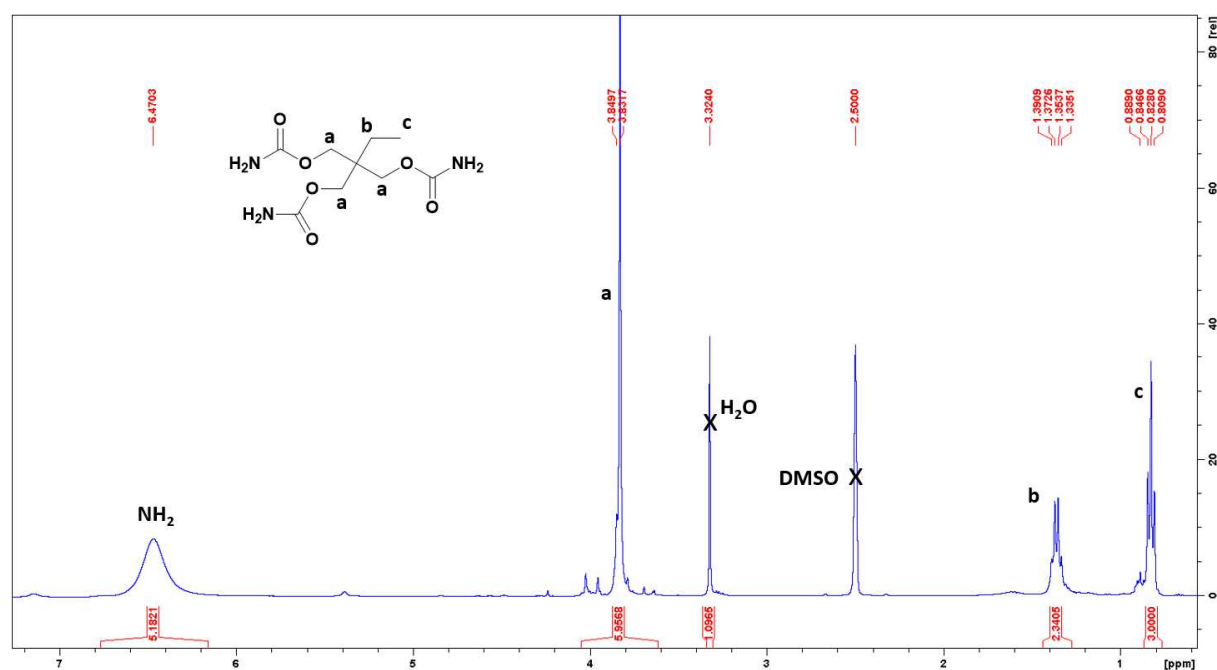


Figure S3 :  $^1\text{H}$  NMR spectrum in  $\text{DMSO-d}_6$  of the purified product

### 3. FTIR-ATR kinetic analysis for the direct observation of the suspected iminium intermediate

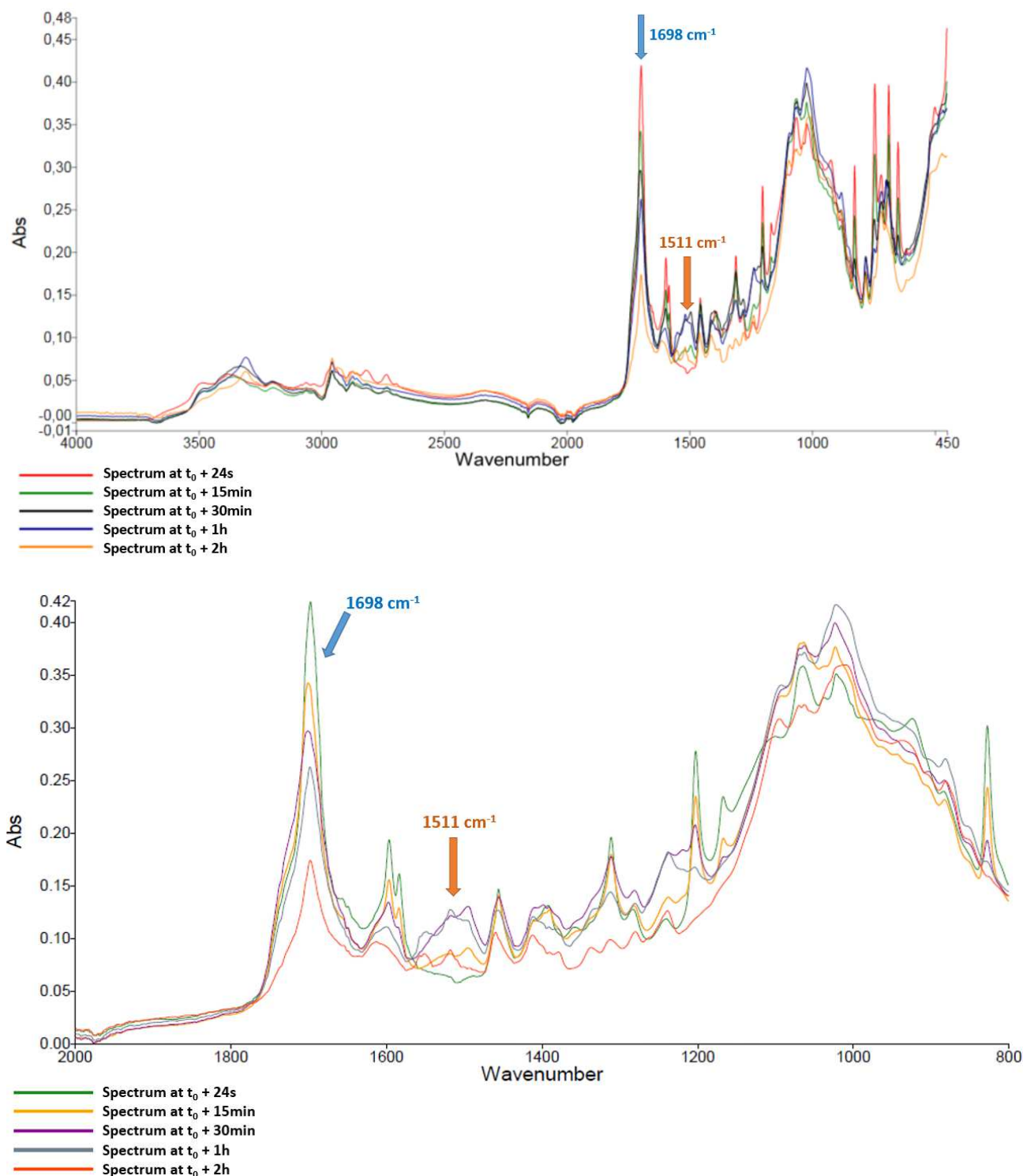


Figure S4 : FTIR-ATR analysis of the reaction between ethyl carbamate and benzaldehyde at 100°C, showing stacked spectra at different times, with a zoom on the zone of interest.

The experiment was run in Attenuated Total Reflectance (ATR) mode using the UATR 2 device from Perkin-Elmer equipped with a heated top plate. As expected, the decrease in the signal at 1698 cm<sup>-1</sup>

corresponding to the carbonyl vibration of the aldehyde can be observed. This signal, together with the carbonyl from ethyl carbamate initially around  $1710\text{ cm}^{-1}$ , never completely disappears because of the contribution of the formed urethane groups in the same carbonyl area during the reaction. However, most of the characteristic bands of benzaldehyde tend to strongly decrease with time, suggesting a possible partial evaporation of this compound, and therefore making this analysis particularly difficult to interpret. Still, the formation of urethanes is also confirmed by the appearance of an NH band at  $3310\text{ cm}^{-1}$  that is clearly visible after 1 or 2 h.

Small band at  $1495$  and  $1511\text{ cm}^{-1}$  also caught our interest. Indeed, they appear during the first moments of the reaction and then fade away as the reaction approaches to completion. This behaviour is typical of a reaction intermediate. Moreover, such wavenumbers are theoretically coherent with the vibration of an iminium-like structure.

#### 4. Evidences of the presence of iminium intermediate's existence: complete NMR spectra of the reaction's raw product.

a/  $^1\text{H}$  spectrum

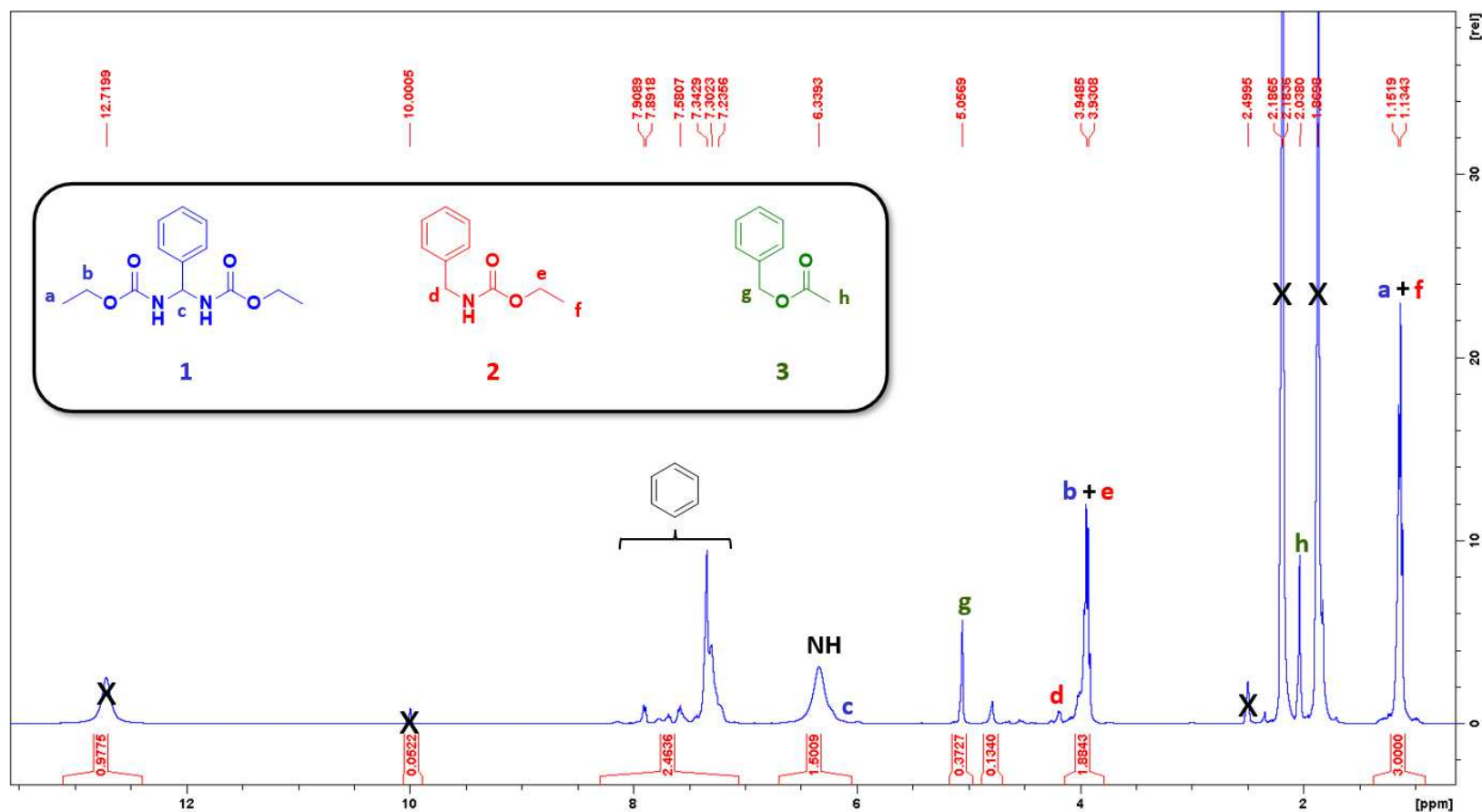


Figure S5 :  $^1\text{H}$  NMR spectrum in DMSO- $d_6$  at room temperature of the raw products of the CA reaction between ethylcarbamate and benzaldehyde in presence of STAB. Crossed signals are due to the presence of acetic anhydride in the raw sample

## b/ $^{13}\text{C}$ spectrum

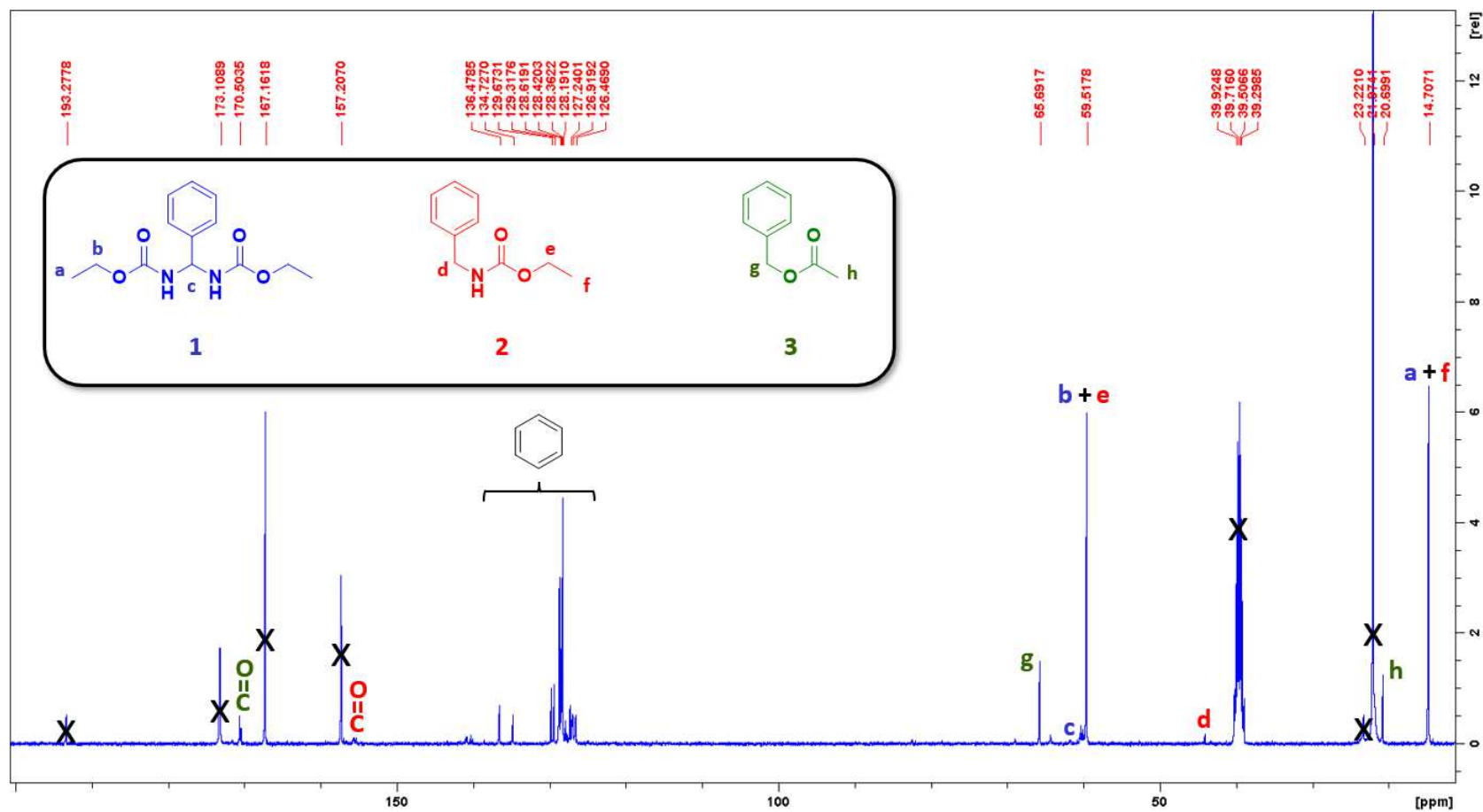


Figure S6 :  $^{13}\text{C}$  NMR spectrum in DMSO- $d_6$  at room temperature of the raw products of the CA reaction between ethylcarbamate and benzaldehyde in presence of STAB. Crossed signals are due to the presence of acetic anhydride in the raw sample

c/ COSY spectrum

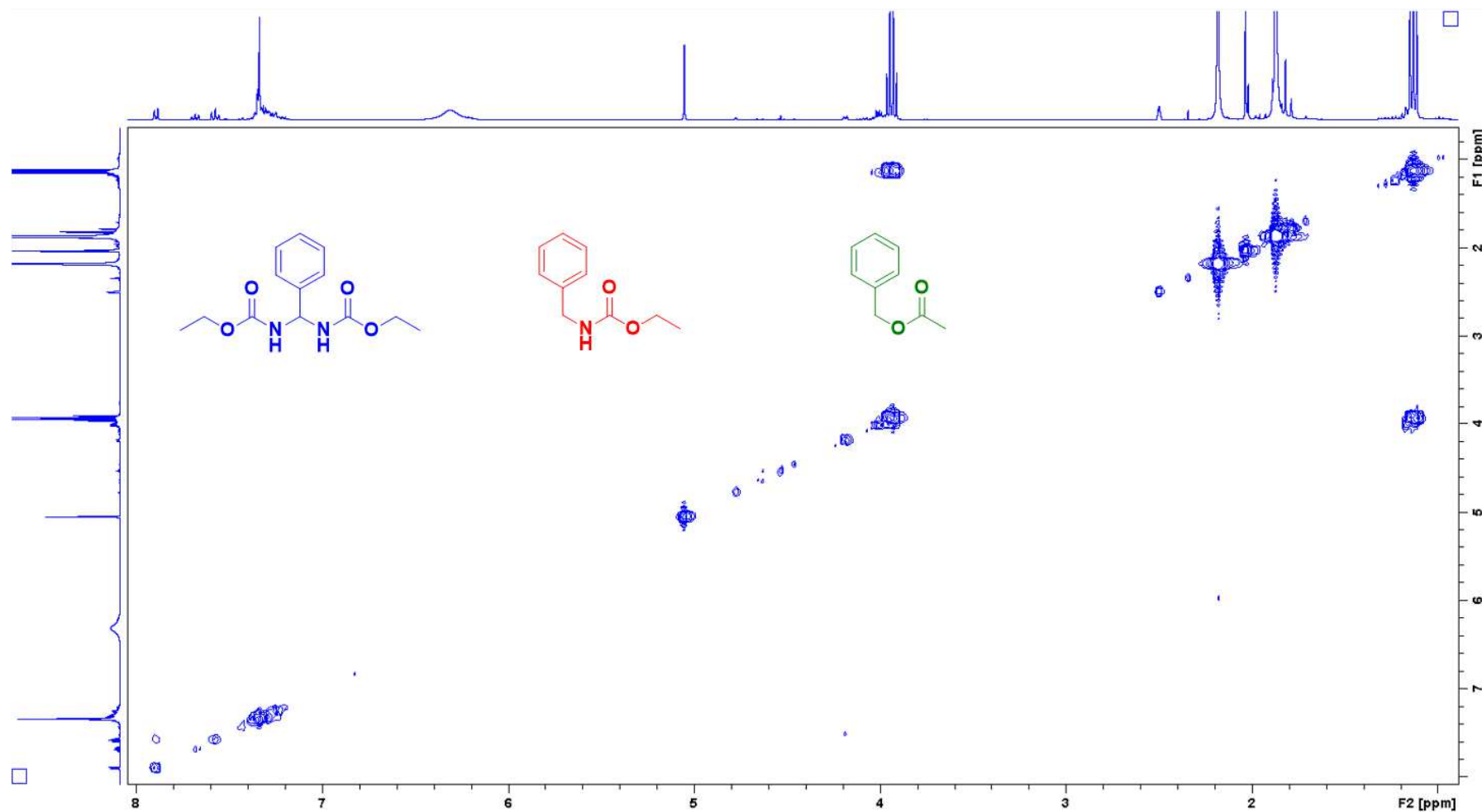


Figure S7 :  $^1\text{H}$ - $^1\text{H}$  homonuclear correlation spectrum (COSY) in DMSO- $d_6$  at room temperature of the raw products of the CA reaction between ethylcarbamate and benzaldehyde in presence of STAB.

d/ HSQC spectrum

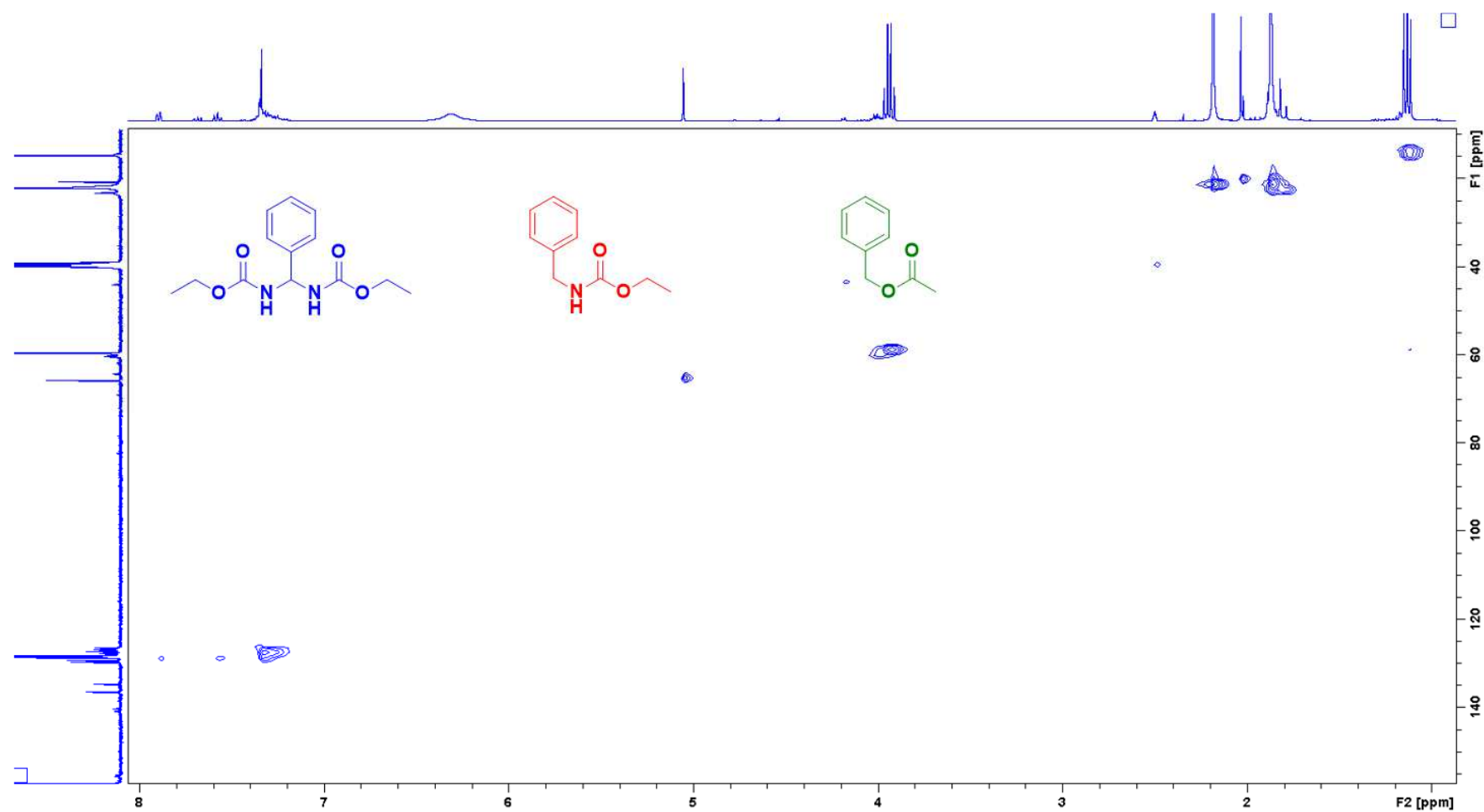


Figure S8 :  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear spectrum (HSQC) in  $\text{DMSO-d}_6$  at room temperature of the raw products of the CA reaction between ethylcarbamate and benzaldehyde in presence of STAB.

e/ HMBC spectrum

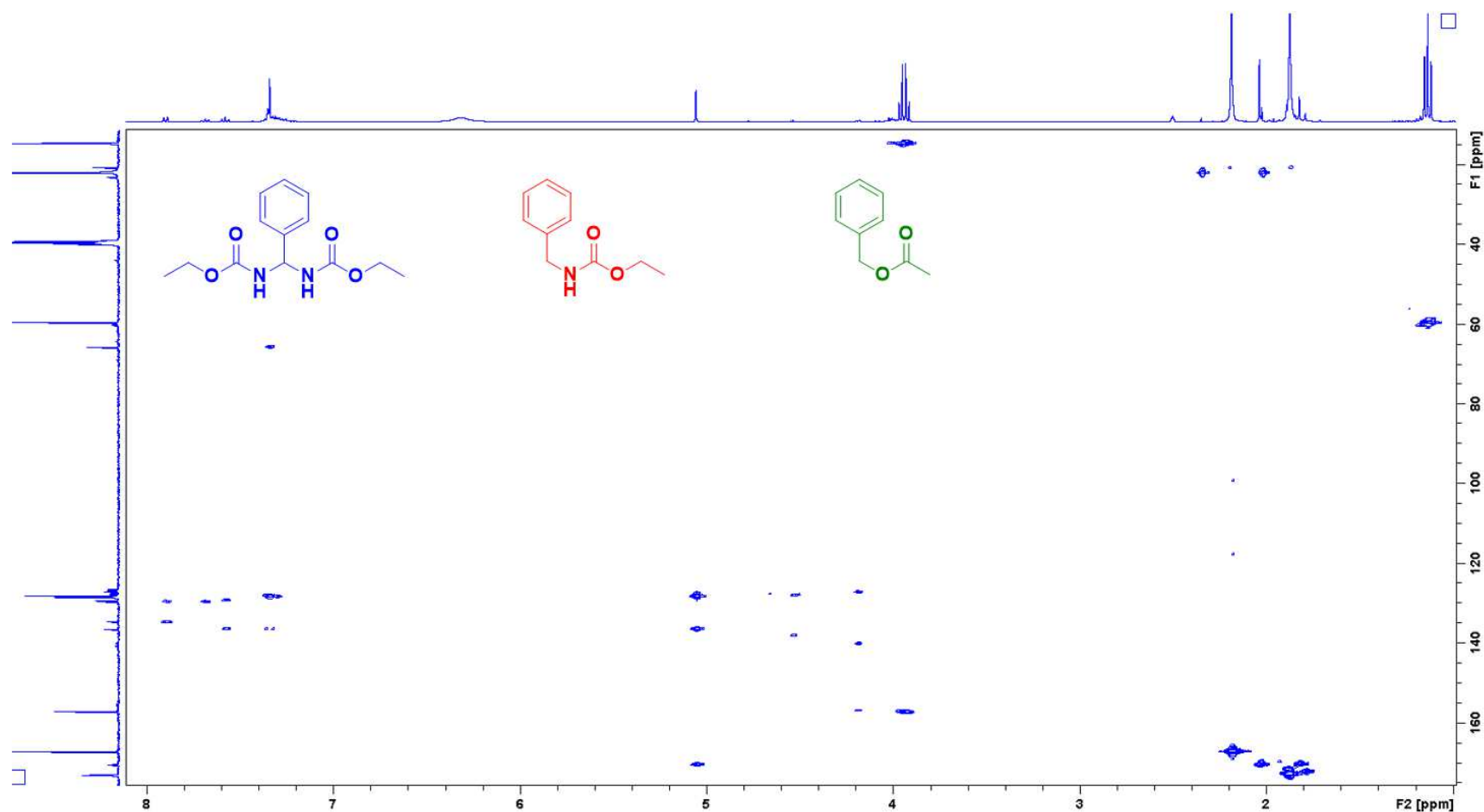


Figure S9 :  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear spectroscopy (HMBC) in  $\text{DMSO-d}_6$  at room temperature of the raw products of the CA reaction between ethylcarbamate and benzaldehyde in presence of STAB.



## 5. MALDI-TOF analysis of the linear NIPU oligomer obtained from the CA reaction between benzaldehyde and ethylene dicarbamate.

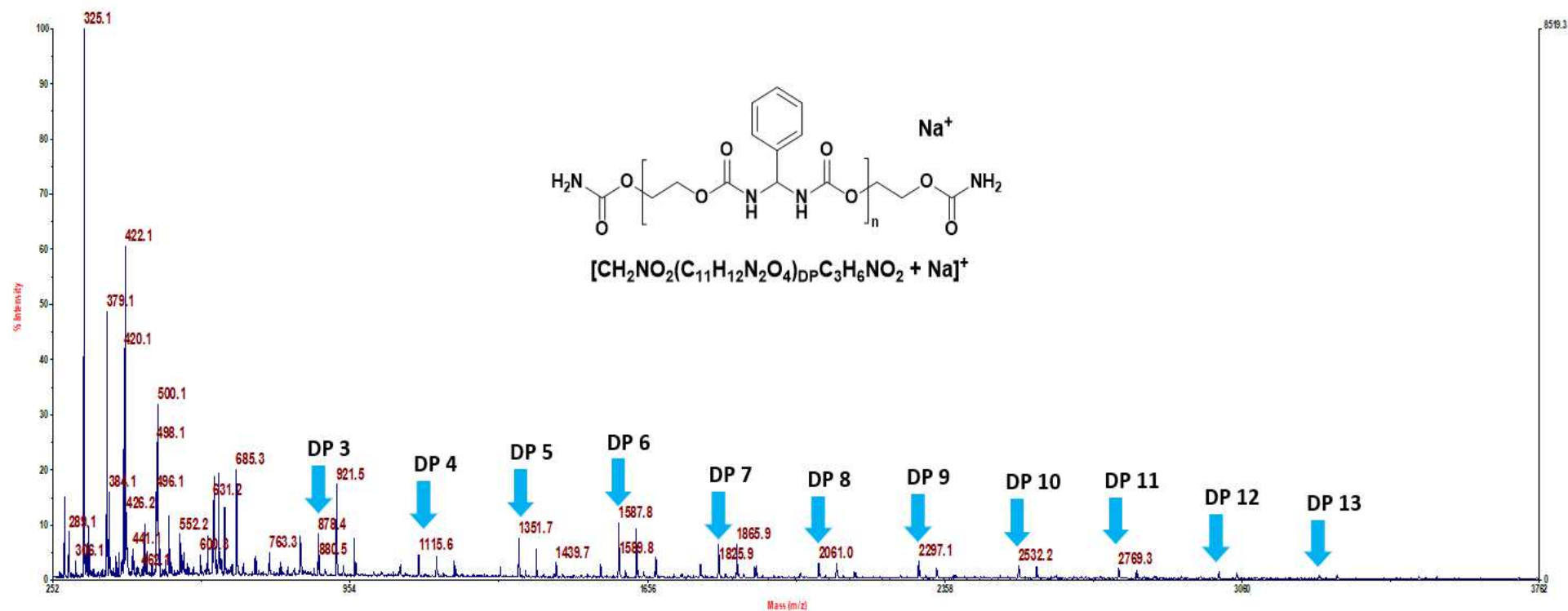


Figure S10 : MALDI mass spectrum of the NIPU oligomers obtained from ethylene dicarbamate and benzaldehyde

## 6. Comparison between compounds synthesized with or without acetic anhydride

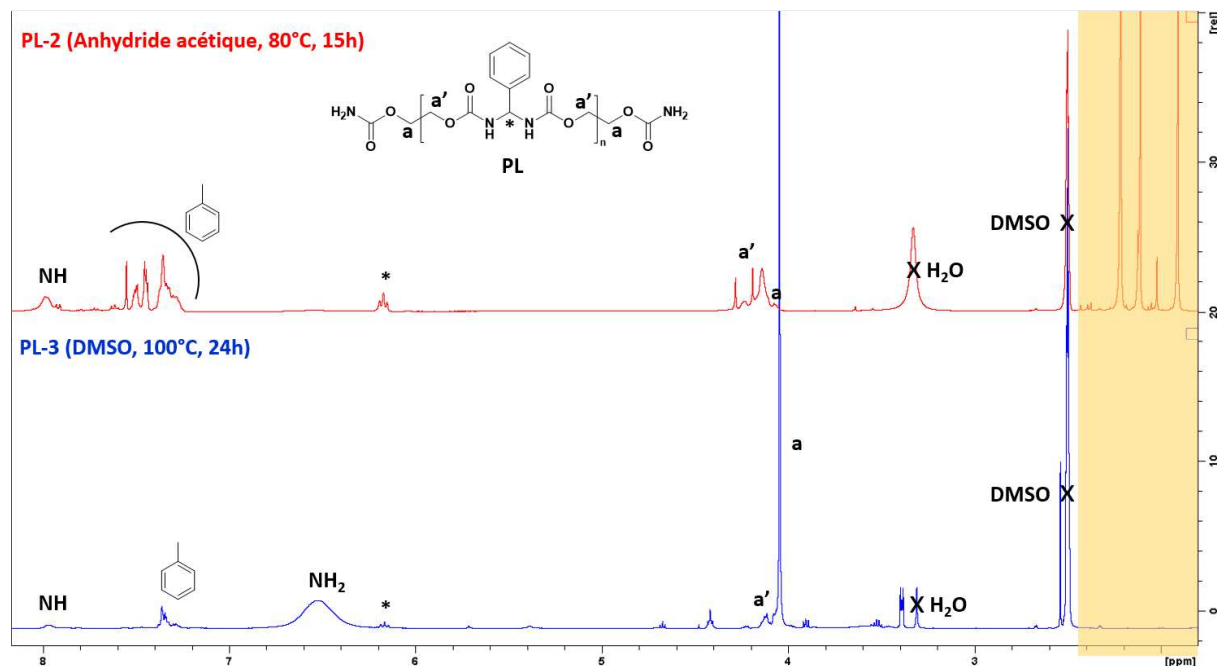


Figure S11 – Comparison of the  $^1\text{H}$  NMR spectra (DMSO- $d_6$ , 25°C) of compound PL-2 (synthesized in solution in acetic anhydride, 80°C) and of the soluble fraction of compound PL-3 (synthesized in solution in DMSO, 100°C, without acetic anhydride) showing the clear difference in the  $\delta$  area below 2,5 ppm

## 7. Thermal degradation of primary carbamate functions

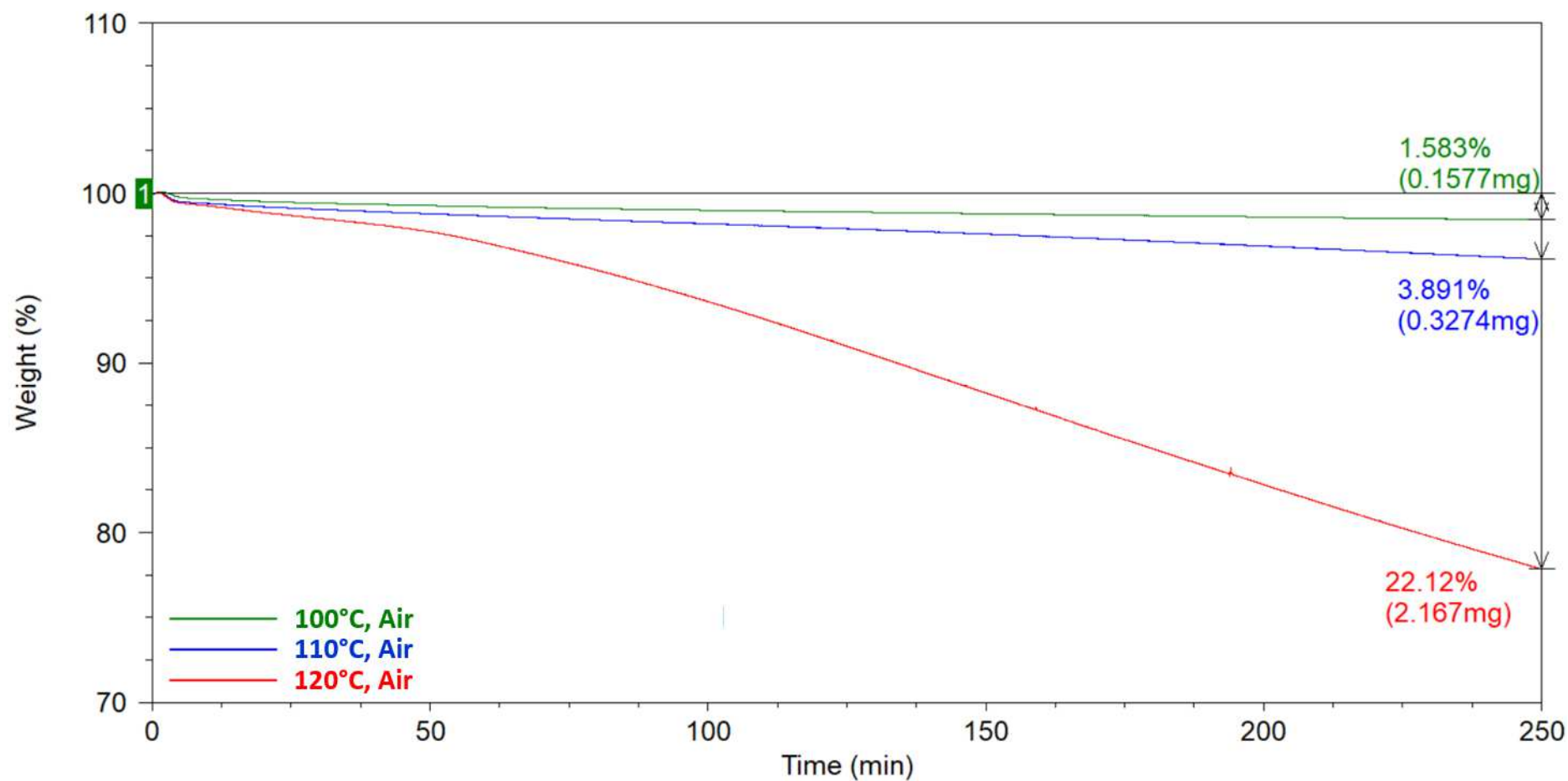


Figure S12 : TGA thermogram of methyl dicarbamate at different isotherms in air

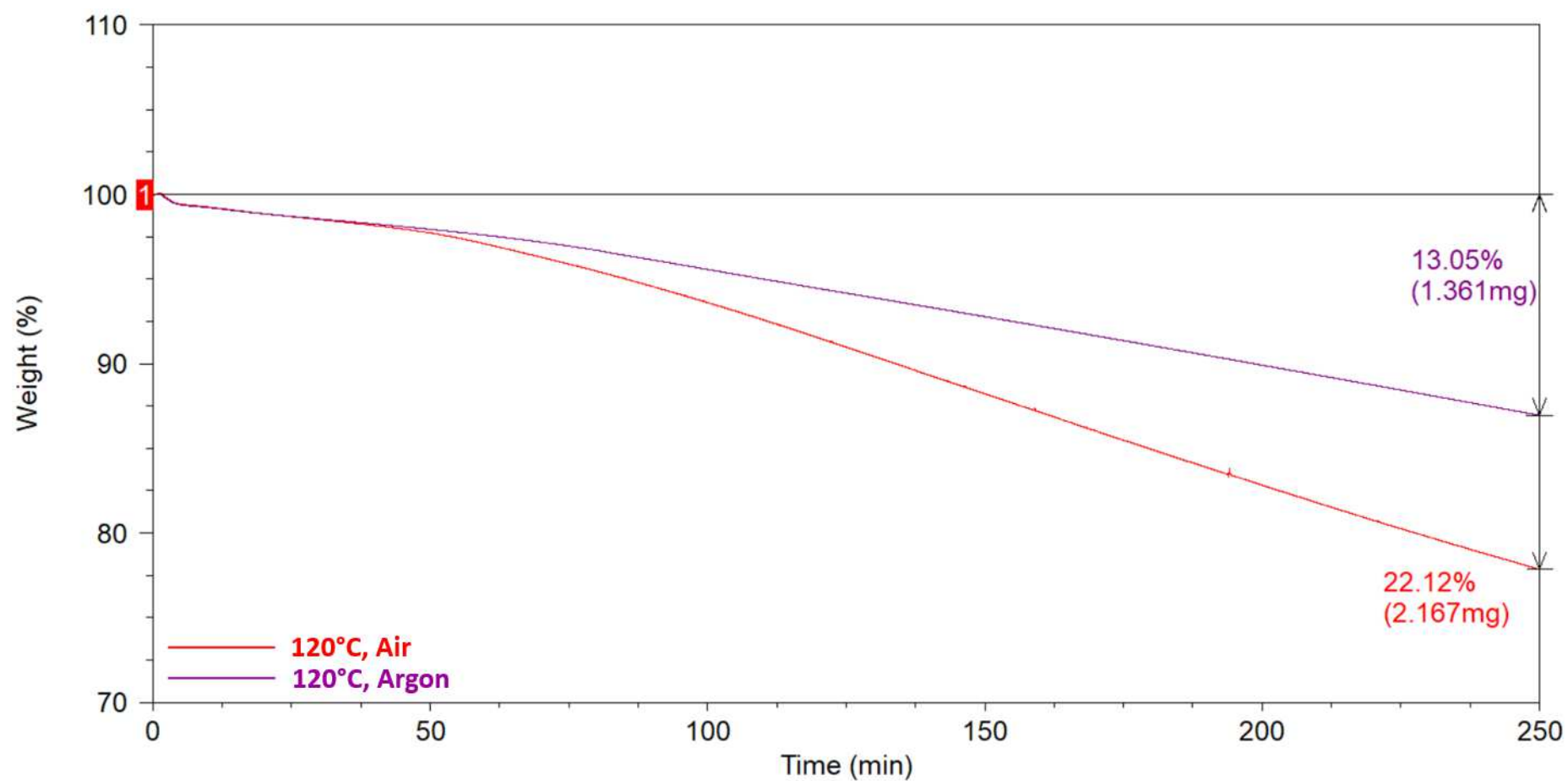


Figure S13 : TGA thermogram of methyl dicarbamate at a 120°C isotherm in air and inert atmosphere

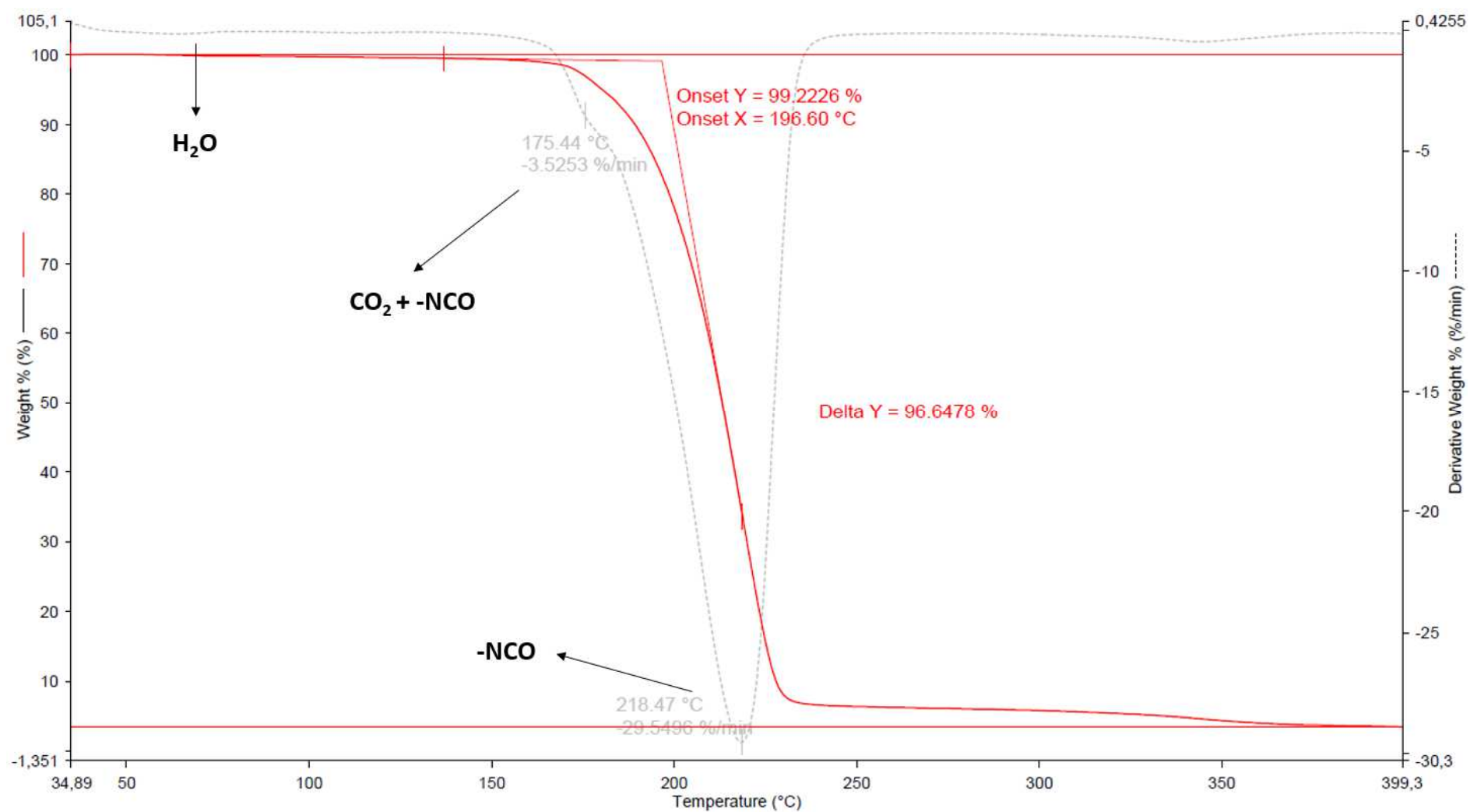


Figure S14 : TGA / FTIR coupling analysis of methyl dicarbamate in air, showing the TGA thermogram (red curve) as well as its derivated curve (gray)

## 8. Thermal properties of NIPU networks

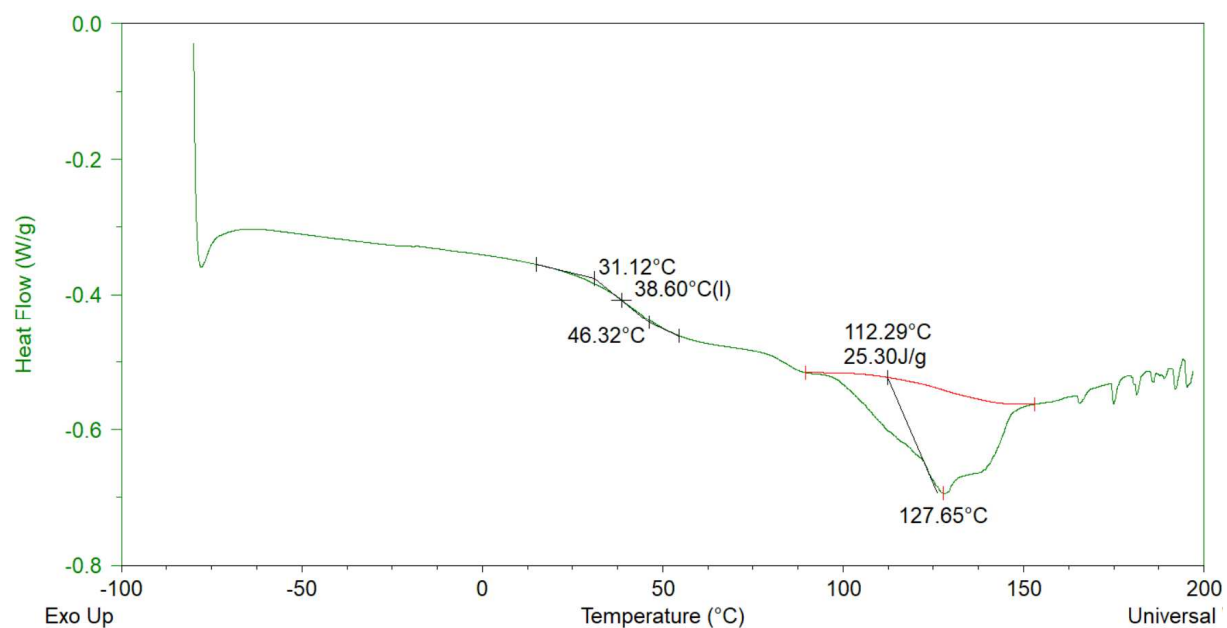


Figure S15 : DSC thermogram of NIPU network 1 (IP = 9 %)

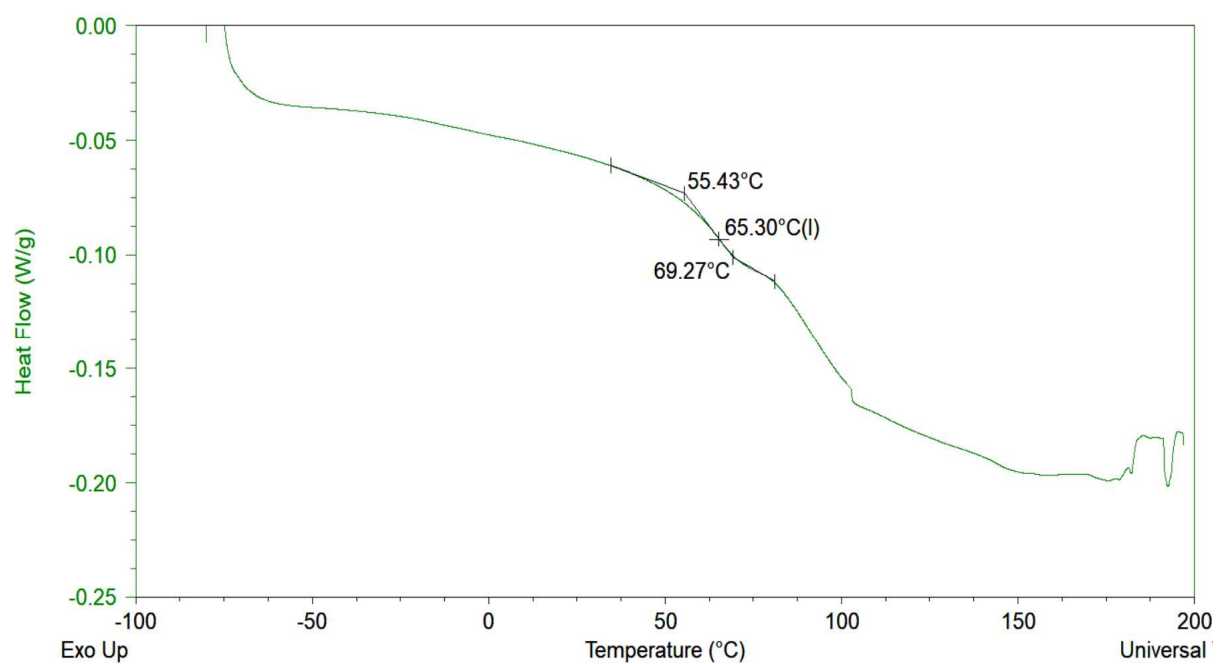


Figure S16 : DSC thermogram of NIPU network 8 (IP = 82 %)