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Fatima-Zohra Belmokaddem, Julie Dagonneau, Julien Lhomme, Romain Blanc, Azucena Garduno-Alva, et al.. Novel nucleophilic/basic and acidic organocatalysts for reaction between poorly reactive diisocyanate and diols. *Designed Monomers and Polymers*, 2016, 19 (4), pp.347-360. 10.1080/15685551.2016.1152545 . hal-01397183

HAL Id: hal-01397183

<https://hal.science/hal-01397183>

Submitted on 5 Mar 2019

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**Novel nucleophilic/basic and acidic organocatalysts
for reaction between poorly reactive diisocyanate and diols**

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Novel nucleophilic/basic and acidic organocatalysts for reaction between poorly reactive diisocyanate and diols

Abstract

Original basic or acidic organic compounds derived from guanidine or phenyl phosphonic acid were specifically designed and tested as new catalysts for the bulk synthesis of polyurethane prepolymers from a precursor system with particularly low reactivity (secondary alcohol + aliphatic isocyanate at low temperature). Both families showed interesting catalytic activities at 60°-80°C, but must nevertheless be used in much higher amounts (1 mol%, i.e. between 0.15 and 0.50 wt%) than traditional metal-based catalysts. The efficiency of guanidine derivatives seems to be related to their nucleophilicity, whereas that of phosphonic acid derivatives depends on their acidity. However the solubility of the considered species in the reactive medium also plays a major role.

The water/alcohol selectivity of the catalysts, especially at room temperature, was then examined as an additional criterion. Guanidines are not selective and favor the reaction of isocyanate groups with water as much as that with alcohols. Phenyl phosphonic acid derivatives are more selective, and particularly pentafluorophenyl phosphonic acid displays a remarkable catalytic activity together with an acceptable selectivity and could represent an interesting and safer alternative to toxic tin and mercury derivatives for many industrial polyurethanes.

Keywords : polyurethane; prepolymers; organocatalysis; guanidine; phenylphosphonic acid; water/alcohol selectivity

Introduction

Polyurethanes (PUs) constitute an important class of polymers with widespread application (foams, adhesives, coatings, elastomers, materials for aeronautics industry...).[1-5] To date, the most straightforward route for their preparation, based on the pioneer work of Bayer, is the reaction between diisocyanates and diols, often in presence of a catalyst.[6,7] Nowadays, two types of metal-based catalysts are mainly used in the polyurethane industry: tin (e.g. dibutyltin dilaurate, DBTDL) [8-12] and mercury (such as [bis(phenyl mercury) dodecenyl succinate or bis(*t*-butyl mercury) dodecenyl succinate]) [13,14] compounds. The former present exceptional catalytic activity, and the latter are ideal latent catalysts which allow for more time to handle the formulation. However, the use of tin and mercury derivatives will be restricted in a near future for environmental reasons.[15-18] As an alternative, less toxic organometallic catalysts such as bismuth, aluminum, zirconium and zinc derivatives were proposed,[19-21] but none of them appears to be entirely satisfactory in terms of both reaction rates and molar masses. The intensive research in the field of organocatalysis during the last years has led to the design of a number of catalysts offering new green alternatives to traditional organometallic catalysts:[22-26] very recently an interesting review gathered the main results newly obtained on this subject.[27]

The most efficient small organic molecules, able to catalyze the synthesis of PUs, are mostly organic bases and/or nucleophiles (see **Scheme 1**). Tertiary amines such as 1,4-diazabicyclo[2,2,2]octane (DABCO), N-alkyl morpholines and amidines (e.g. 1,8-diazabicyclo[5,4,0]undec-7-ene, DBU) have been shown to accelerate the reaction between diols and diisocyanates, however their overall efficiencies remain low compared to tin-catalysts.[28] Landais and Cramail have disclosed very interesting results showing the enhanced catalytic activity of bicyclic pentaalkylated guanidines (MTBD),[29,30] leading to PU molar masses similar to those obtained with tin catalysts. Recently, Destarac and al. described the catalytic activity of 1,3-bis-(di-*tert*-butyl)imidazole-2-ylidene (*t*BuNHC) for the polymerization of aliphatic diisocyanates and diols, using relatively low catalyst loading and mild conditions.[31] However, all these studies are exclusively devoted to primary alcohols, which are the most reactive towards isocyanates. In contrast, secondary alcohols are much less reactive, although this family of alcohols such as poly(oxypropylene) polyols are widely used in polyurethane industry, and very little literature addresses this issue in terms of innovating catalysts.

[Scheme 1 near here]

Surprisingly, only a few studies concern the use of organic acids as catalysts for the synthesis of PUs. Preliminary results have been reported by Nordstrom (organic acids) [32] and by Yezrielev (with a disulfonic acid) [33] for the activation of the reaction between isocyanates and alcohols. However, in both cases, the results are less favorable compared to those observed with tin-based catalysts. Recently, a catalyst screening study of organic acids (sulfonic acids, carboxylic acids, phosphonic acids) was reported by Hedrick.[34,35] Among them, sulfonic acids exhibit very interesting activities at room temperature and were found to compete with DBTDL, both in terms of efficiency and of PUs molar mass. Interestingly, Hedrick has demonstrated that no PU degradation was observed when acidic catalysts were used, contrary to what could be observed after several days when strong bases were used.[34,35]

Herein we report the evaluation of novel organocatalysts (guanidine and acidic phosphorus derivatives) for the polymerization reaction of isophorone diisocyanate (IPDI) and poly(oxypropylene) macrodiols, monomers which often require harsh reaction conditions and/or large catalyst loading.

Experimental

Materials

Isophorone diisocyanate (IPDI) and α,ω -dihydroxy poly(oxypropylene) (PPG-2000) were gifts from Allrim-Juxta (Audincourt, France). The hydroxyl number of the macrodiol was estimated as $I_{OH} = 56$ mg KOH/g using both chemical titration with acetic anhydride (French standard NF T 52-112) and 1H NMR. Tetramethylguanidine (TMG), *t*-butyl tetramethylguanidine (*t*-BuTMG), phosphonic acid, ethyl phosphonic acid, vinyl phosphonic acid, phenyl phosphonic acid and trifluoromethane sulfonic acid (triflic acid), as well as 1-methoxy-2-propanol (PGME) and di(propylene glycol) dimethyl ether (DPGDME) were purchased from Aldrich France. 1-butyl-2,3-dicyclohexyl-1-methylguanidine (Cy₂MeBuG), 1-cyclohexyl-2,2,3,3-tetrapropylguanidine (CyPr₄G) and 1-octyl-2,2,3,3-tetramethylguanidine (OctTMG) were synthesized by Bluestar Silicones (Saint-Fons, France). Allyl phosphonic acid was obtained from Specific Polymers (Castries, France). All the other catalysts, i.e. perfluorophenyl phosphonic acid, mesityl phosphonic acid, mesityl phosphinic acid and 3,5-bis(trifluoromethyl)phenyl phosphonic acid (“CF₃ phenyl”) were synthesized at the LHFA. Full experimental procedures and characterization data for non-commercial derivatives can be

found in the **supporting information**. The chemical structures of all the guanidine and acidic phosphorus catalysts are given in **Schemes 2 & 3**.

All solvents and reagents were used as received.

[Scheme 2 near here]

[Scheme 3 near here]

Kinetic studies

PPG-2000 was reacted in bulk with excess IPDI (initial ratio $[\text{NCO}]/[\text{OH}] = 2.00$) at various temperatures (20 - 80°C) and using different amounts of catalysts (1 mol%, i.e. between 0.15 and 0.50 wt% depending on the chemical structure), leading to bis(isocyanato-terminated) polyurethane prepolymers. A typical experiment can be described as follows: the PPG macrodiol was first systematically dried under vacuum at 100 °C for 3 h; whereas the NCO index of IPDI was also systematically checked by titration (see below). When a catalyst was used, an appropriate amount was mixed with the macrodiol. Since the reaction between IPDI (~66 g, i.e. ~0.594 mol NCO) and PPG-2000 (~300 g, i.e. ~0.299 mol OH) was always very slow at room temperature, and since these compounds were rather fluid they could then be pre-mixed in a beaker under magnetic stirring. This mixture was finally poured in a thermo-regulated 1 L jacketed reactor under nitrogen blanket. This reactor was equipped with a mechanical stirrer (300 rpm) and a bottom outlet gate was used for easy sampling.

In the case of water/IPDI reactions, a solvent was added in order to maintain the OH-concentration similar to that of the bulk PPG-2000/IPDI experiments (ca 0.82 mol/kg). The OH equivalent weight is indeed 9 g/mol OH for water, vs 1002 g/mol OH for the macrodiol. Di(propylene glycol) bis(methyl ether) (DPGDME) was chosen for this purpose as it could provide the medium with a polarity rather similar to that of the polyether chain. The water content of this solvent was 0.14 wt%. In a typical experiment, DPGDME (290 g) was mixed with water (2 g), and then the blend was homogenized 1 night at room temperature. A proper amount of this mixture was then added to a pre-weighed amount of IPDI (~60 g) in a beaker, in order to obtain $[\text{OH}]/[\text{NCO}] = 0.5$. The blend was homogenized once more with a mechanical stirrer, and the catalyst was then added. The reaction mixture could then finally be poured into the thermo-regulated reactor.

Isocyanate titration

The kinetics were estimated by monitoring the amount of residual NCO groups. Isocyanate functions were determined following the French standard AFNOR NF T 52-132 by reacting

them with an excess of N,N-di(*n*-butyl) amine and back-titrating the excess amine with 1N HCl in anhydrous acetone, using bromocresol green as indicator. A blank titration was also carried out without isocyanate, using precisely the same amount of N,N-di(*n*-butyl) amine.

Size exclusion chromatography (SEC)

Molar mass distributions were assessed by Size Exclusion Chromatography, SEC, using tetrahydrofuran (THF), at 35 °C as eluent. The THF flow rate was 1.0 mL/min. Analyses were run on a Viscotek chromatograph equipped with 3 Styragel HR 4E columns; detectors consisted of a differential refractometer VE3580 and a Dual T60A detector (combining a right angle light scattering detector and a viscosimeter).

¹H and ¹³C Nuclear Magnetic Resonance

The chemical structures of the prepolymers were determined by ¹H or ¹³C NMR spectroscopy performed on a Bruker DRX 400 spectrometer operating at 400 (¹H) or 100 (¹³C) MHz. Samples were prepared in DMSO-d₆ or CDCl₃.

Results and discussion

New guanidine derivatives catalysts

Following the promising results obtained by Alsarraf et al [29,30] and by Maliverney [36], the kinetics of the reaction between IPDI and PPG-2000 was first monitored in the presence of 1 mol% of catalyst (with respect to the NCO groups, i.e. between 0.19 and 0.50 wt%) chosen among five different guanidine derivatives with different basicity (see **Table 1 in supporting information**). At 60 °C, the NCO conversion curves obtained (x_{NCO} vs time) are represented in **Figure 1**.

[Figure 1 near here]

First, although the amount of added catalyst is non-negligible, it appears that none of the tested species displays a real efficient catalytic activity for the considered reactive system. Typically it would take only about 40 min to reach complete conversion ($x_{\text{NCO}} = 0.5$) at 45 °C using 0.017 mol% of dibutyl tin dilaurate;[37] whereas here only 3 guanidines (TMG, *t*BuTMG and OctTMG) allow to reach complete NCO conversion within 1 day or so (**Figure 1a**). Moreover, the conversion obtained with *t*BuTMG clearly exceeds 0.5 (the theoretical maximal conversion if only urethanes were formed), denoting that this catalyst probably induces secondary reactions such as the formation of uretidione dimers, isocyanurate trimers, or allophanate branching points.

A closer look at the relative activities of the different guanidines used is given in **Figure 1b**. The most hindered guanidines, CyPr₄G and Cy₂MeBuG, showed a poor ability to catalyze the polymerization reaction, indicating that the catalytic activity should be related to the nucleophilicity instead of the basicity. Indeed, with the less hindered compounds, therefore more nucleophilic, the kinetics of the reaction increased notably. However, the case of TMG is particular since it bears a labile hydrogen atom (in fact, Cy₂MeBuG also has one, but it is a secondary conjugated amine and this proton should not be very reactive towards isocyanates or should only lead to an equilibrium). TMG can therefore easily react with the diisocyanate IPDI to yield a stable adduct (note that other guanidines, not bearing labile protons, are also susceptible to yield 2:1 adducts with a heterocyclic triazinedione moiety, but this was not observed for the case of IPDI and *t*BuTMG because of steric hindrance [38]). Apart from consuming a slight amount (1 % at the most) of isocyanate functions, the formation of the IPDI-TMG adduct could also participate in the catalytic activation. This was already observed by Alsarraf for other guanidines,[30] but in this case the guanidines had no labile hydrogen and the adducts were rather pseudo isocyanurates involving 2 isocyanate molecules; moreover the actual catalyst was found to be the guanidine that was regenerated in the presence of OH groups above 60 °C. In the present work the bis(urea) adduct was thus synthesized by reacting stoichiometric amounts of IPDI and TMG in bulk at room temperature ([NCO]/[NH] = 1, see **Scheme S1** in **supporting information**). A solid product was rapidly obtained that was then characterized by NMR spectroscopy (¹H and ¹³C). In contrast to this quasi-instantaneous process, the reaction between aliphatic isocyanates and Cy₂MeBuG takes several hours in bulk at room temperature, and the catalytic activity of the IPDI-(Cy₂MeBuG)₂ adduct was not studied.

In order to be able to properly assess the NMR signals detected in the various prepolymers, a model reaction was first conducted between IPDI (1 eq.) and 1-methoxy-2-propanol (PGME, 1 eq.), i.e. with [NCO]/[OH] = 2 (20 °C, catalyst 0.2 mol% phenylmercury neodecanoate). The residual NCO groups were then neutralized using an excess of di(*n*-butyl) amine (DBA). The reaction is depicted in **Scheme 4**, and the resulting ¹H NMR spectrum is shown in **Figure 2**. This allows to associate signals between 6.4 and 7.2 ppm to the NH groups of the urethane functions, whereas urea NH groups appear between 5.4 and 6.0 ppm. The urea comes mainly from the capping reaction with DBA; however, the starting PGME also contains about 0.015 wt% of water that could react with IPDI leading to additional alkyl urea functions exactly in the same δ range; this could account for the slightly higher integration of the urea peak (1.098 instead of 1.00 for the urethane).[39]

[Scheme 4 near here]

[Figure 2 near here]

NMR-spectra of the pure IPDI-TMG adduct and of the IPDI-PPG prepolymer synthesized in the presence of 1 mol% of TMG at 60 °C are represented in **Figure 3**. The spectrum of the polyaddition product of IPDI and PPG-2000 obtained in the presence of a large amount (~32 mol% / NCO) of TMG was added for comparison.

[Figure 3 near here]

In the prepolymer spectrum, several signals appear in the urea proton range between 5.4 and 6.0 ppm. They might be due to the partial hydrolysis of NCO groups by moisture brought by the PPG-2000 macrodiol or the highly hygroscopic guanidine catalyst. But no trace of the adduct can be detected in the prepolymer spectrum; however, only 1 mol% of TMG was added and even if this compound was formed, it might be in too low quantities to appear clearly in this spectrum. In contrast, the spectrum of the polyurethane synthesized in the presence of non-negligible amounts of TMG clearly displays the urea peaks associated with this adduct between 6.1 and 6.4 ppm, even though large amounts of alcoholic protons were also present and moreover supposed to be activated by TMG. This confirms a competition between the nucleophilic and basic activations that can be attributed to guanidine compounds as already mentioned by Alsarraf.[29]

The use of the adduct (pre-dissolved in 1 mL THF before addition to the macrodiol) as catalyst in the IPDI-PPG reaction resulted in a clear enhancement of the kinetics, as shown in **Figure 4**. Its catalytic efficiency seems rather similar or even a little higher than that of TMG under these conditions (60 °C); the shapes of all the curves are also quite similar and do not particularly suggest a regeneration of the parent guanidine in the case of the adduct, contrary to Alsarraf's latent catalysts.[30] (It should be noted that although a second order is very classically observed for catalyzed isocyanate-alcohol reactions, here such a kinetic analysis could not be precisely performed, since in bulk the process is not isothermal as the reaction is exothermic).

[Figure 4 near here]

At 80 °C though, the situation is a little bit different. **Figure 5a** shows that the order of catalytic efficiency is about the same as that found at 60 °C, although the various kinetic curves are closer to each other than at lower temperature. But under these conditions almost every tested catalyst finally leads to conversions higher than 0.5; i.e. while catalyzing the isocyanate-alcohol reaction, they probably all induce side reactions of the NCO functions at

the same time. Moreover the time to reach 0.5 is very long (10 h or more) compared to classical metal catalysts. The kinetics recorded for DBTDL at 80°C was added in Figure 5 for comparison, but even using only 0.0056 mol% (~ 0.006 wt%), i.e. 180 times less than the tested guanidines, the reaction was incomparably faster. Together, these 2 observations suggest that none of the tested guanidine derivatives appears to be a very suitable catalyst for the considered “low reactive” polyurethane system (aliphatic isocyanate / secondary alcohol at temperatures below 100 °C).

[Figure 5 near here]

Furthermore in **Figure 5b**, it appears that the curve associated with the adduct has a rather sigmoidal shape that is not observed with simple guanidines. This might reveal a more complex mechanism in this case. First, a possible thermally induced, at least partial re-dissociation of the adduct to yield free TMG molecules could occur at 80 °C (possibly activated by the presence of OH groups). Guanidines and amidines have indeed been mentioned as blocking agents for isocyanates, but this remains rather occasional.[38,40,41] Moreover a comparison between **Figure 4 and 5** suggests that the adduct has in fact rather similar effects on the kinetics at the beginning of the reaction, although the conditions are different (0.1 mol%, 60 °C vs 1 mol%, 80 °C). But the final conversions are nevertheless very different, since x_{NCO} almost stops increasing after about 3 hours in the first case, whereas it keeps on increasing to reach 0.5 and above in the second case. This could mean that only a very small fraction of this catalytic compound is in fact soluble in the reactive medium at the beginning, about the same in both cases; but as isocyanate functions are consumed and more and more urethane bonds are formed, this solubility might increase; and finally at 80 °C and starting with higher amounts of IPDI-TMG adduct, a higher fraction of the catalyst could become active above $x_{\text{NCO}} \approx 0.2$.

Guanidine derivatives are thus interesting organocatalysts for the synthesis of polyurethanes through the isocyanate-alcohol addition reaction, with a much lower toxicity than the usual metal catalysts. But they are not exceptionally efficient, especially as far as systems with low reactivity are concerned. Moreover, they also catalyze the isocyanate-water reaction, which is an important drawback for their use in the preparation of solid polyurethane materials, especially if they are transparent. In agreement with this, it can be noted that guanidines have been mentioned as good accelerators for moisture-curable systems.[42] Considering that this would not be sufficiently satisfying from an industrial point of view, and

taking into account the recent studies of Sardon et al,[34,35] new attempts were made with a family of organic acids derived from phenyl phosphonic acid.

New acidic phosphorus derivatives catalysts

Sardon et al recently obtained interesting results for the catalysis of the reaction between poly(ethylene glycol) and hexamethylene diisocyanate (HDI) using sulfonic acids and especially triflic acid.[34] From molecular modeling, ternary adducts between acid, isocyanate and alcohol were assumed to be formed. Furthermore the efficiency of such derivatives was shown to be related to the strength of the acid as well as to the nucleophilicity of the conjugate base. Since triflic acid even proved to be an efficient catalyst for the bulk polyaddition reaction of HDI with PPG ($M_n = 1000 \text{ g}\cdot\text{mol}^{-1}$) at 60 °C, it was obviously very interesting to test it under our own experimental conditions. Surprisingly, a comparatively low activity was found for both carboxylic acids (acetic and trifluoroacetic acids) and diphenyl phosphate.[34] However, strong phosphonic acids such as phenyl phosphonic acid or its derivatives have never been tested, and therefore we have decided to evaluate their catalytic activity, first at 60°C (see **Figure S1** in **supporting information**) then at 80°C.

Figure 6 shows all the kinetic curves obtained for the bulk reaction of IPDI with PPG-2000 ($[\text{NCO}]/[\text{OH}] = 2$) at 80 °C, in the presence of various acidic catalysts (a more complete study with additional catalysts can be found in the **supporting information**, see **Scheme S3 & Figure S2**). Here again the case of DBTDL in very low amounts (0.0056 mol%, i.e. ~0.006 wt%) was added for comparison. It appears first in **Figure 6a** that for all the used catalysts except perfluorophenyl phosphonic acid, the maximal conversion is below or only very slightly above (case of phenyl phosphonic acid) $x_{\text{NCO}} = 0.5$, denoting only few secondary reactions for NCO groups. The case of perfluorophenyl phosphonic acid is strikingly different with a maximal NCO conversion close to 0.8; in this case the final prepolymer was also highly viscous, unlike all the others. Numerous side reactions can thus be suspected (see below).

[Figure 6 near here]

In **Figure 6b**, the initial catalytic activities of all the used compounds can be compared. Most of them are much more efficient catalysts than all the tested guanidines (**Figure 5b**). Among the phenyl phosphonic acid derivatives, a global tendency with some exceptions can be observed: roughly, within this family the efficiency of the catalyst seems to

be directly related to its acidity with the most acidic compounds leading to the highest catalytic activity. This was also observed by Sardon et al. The attractive effect of the phenyl moiety is even enhanced by the presence of fluorine atoms or CF_3 groups, and this seems favorable for the catalytic activity of the considered molecule. However mesityl phosphonic acid ($\text{pK}_a = 2.11$), supposed to be more acidic than ethyl phosphonic acid ($\text{pK}_a = 2.64$), was found less active. It might be because this molecule is sterically hindered and cannot interact easily with isocyanate and alcohol groups to form adducts like in the case of sulfonic acids catalysts.[34]

Although phosphonic acid is also highly acidic, a very low catalytic activity was found for the presently studied system. The high polarity of this molecule that does not display any organic substituents probably lead to a poor solubility in the IPDI/PPG-2000 mixture compared to all the other derivatives, justifying the particularly low efficiency of this catalyst.

Finally triflic acid, although highly acidic and presumably showing sufficient solubility in the reacting medium, also displayed a rather disappointing medium catalytic activity. In Sardon's work,[34] the bulk polyaddition IPDI + PPG-1000 was found completed after about 6 h at 60 °C in the presence of 2.5 mol% triflic acid (with respect to the NCO groups). In our case the maximal conversion $x_{\text{NCO}} = 0.5$ seems to be reached after about the same time at 80 °C, but using only 1 mol% of triflic acid. Both results are thus rather consistent, and the fact that triflic acid does not appear as the best catalyst for the IPDI-PPG reaction is finally rather due to the remarkably high efficiency of phenyl phosphonic acid derivatives.

In dichloromethane solution, Sardon observed well-defined kinetic orders (second order with respect to the alcohol + isocyanate, first order with respect to the acid catalyst). In contrast no clear order with respect to the concentration of the reactive functions was found in our case (bulk reaction, with possibly non-isothermal conditions at the beginning because the reaction is exothermic). Moreover as shown in **Figure 7**, the kinetics are indeed logically enhanced by the increased concentration of phenyl phosphonic acid at 80 °C, but the constants that could be grossly deduced from the first 3 data assuming second order for the reactants do not increase linearly with acid concentration. If the order with respect to phenyl phosphonic acid was 1, the reaction catalyzed with 0.15 mol% catalyst would be much slower.

[Figure 7 near here]

Figure 8 depicts the effect of temperature on the kinetics of the model IPDI/PPG-2000 reactions catalyzed with 1 mol% (with respect to NCO groups) phenyl phosphonic acid or 3,5-bis(trifluoromethyl)phenyl phosphonic acid (“CF₃ phenyl”). Both catalysts present very similar activities, whatever the temperature; the conversion obtained with phenyl phosphonic acid is only generally very slightly higher. The strong electron-withdrawing effect of the trifluoromethyl groups strongly influences the pK_a of the acid (see **Table 2 in supporting information**) but not really the catalytic activity; however it might also be counterbalanced by a negative effect on the solubility of the catalyst in the medium. Quite logically, increases in temperature speed up reactions, however the lack of a well-defined kinetic constant did not allow the strict application of Arrhenius’ law to our data.

[Figure 8 near here]

For some applications, it can be necessary to perform the IPDI-PPG-2000 polyaddition at room temperature, and toxic metal-catalysts, such as tin or mercury derivatives are typically used for such purpose.[43] Replacing these metal catalysts by organic catalysts is now a burning issue. However **Figure 8** shows that although phenyl phosphonic acid seems rather efficient, at room temperature the use of only 1 mol% with respect to NCO groups does not allow to reach full conversion in a reasonable time. Higher amounts, up to 10 mol%, were thus tested. It appears that under such conditions the use of 5 mol% is not really satisfying; only 10 mol% phenyl phosphonic acid allows an immediate and sharp increase in the NCO conversion. Nevertheless, in this case, the maximal $x_{\text{NCO}} = 0.5$ was not reached after 1 day. However, keeping in mind that the gel conversion for the polyaddition of a [A3 + B2] system is about 0.7,[44] gelation of such a reactive system (PPG triol + IPDI) at room temperature could still be obtained within a reasonable time using 10 mol% of phenyl phosphonic acid as catalyst.

In many applications, transparent polyurethane materials are needed, and the reaction between isocyanate functions and water that tends to create CO₂ bubbles is strictly prohibited. Ideally, a catalyst that could enhance the reaction of NCO groups with alcohol while hampering that with water would be desired in this case. Such a catalyst is said to have a good water/alcohol selectivity. In **Figure 9**, a simple comparison was drawn between the final polyurethane prepolymers obtained in bulk at 80 °C, using 1 mol% of 4 efficient catalysts taken among those presented above (*t*BuTMG, TMG, phenyl phosphonic acid and 3,5-bis(trifluoromethyl)phenyl phosphonic acid). Their ¹H NMR spectra clearly show that a large amount of urea protons is present in the case of the guanidine catalysts. The largest amount is

logically obtained with TMG, but even for *t*BuTMG that does not bear any labile proton, urea groups are clearly detected in non-negligible amounts; whereas these protons are almost absent in the case of the phenyl phosphonic derivatives. However all these prepolymers were obtained under the same experimental conditions, starting from the same, similarly dried reagents; it can therefore be assumed that the water/alcohol selectivity of the phosphorus derivatives is much better than that of the guanidines, i.e. that they do not catalyze as much the reaction of NCO groups with adventitious moisture. Since this was particularly interesting from an industrial point of view, further investigation was carried out regarding the kinetics of the reaction between water and IPDI in the presence of these promising new catalysts.

[Figure 9 near here]

Reaction between IPDI and water

For an appropriate comparison with the PPG macrodiol, the kinetics of the reaction between water and IPDI was studied in solution in DPGDME (see experimental part), using from 1 to 10 mol% (0.26 to 2.55 wt%) of phenyl phosphonic acid as catalyst. The conversion of NCO groups was once again monitored *vs* time and the data compared with those recorded for PPG-2000 as plotted in **Figure 10**.

[Figure 10 near here]

Unfortunately, for the 3 tested concentrations the reaction with water is notably fastened by the catalyst, and its kinetics are even more enhanced than that of the urethane formation, especially for low concentrations. Two other efficient organic catalysts, namely perfluorophenyl phosphonic acid and 3,5-bis(trifluoromethyl)phenyl phosphonic acid were tested for comparison but the water/alcohol selectivity in both cases was not better, and in fact it was even worse in the latter case (see **Figure S6** in the **supporting information**). Therefore the use of these phosphorus derivatives for the preparation of solid transparent PU materials, although interesting from an environmental point of view, will probably not avoid the formation of bubbles that can sometimes be bothersome.

The hydrolysis products of IPDI obtained with perfluorophenyl phosphonic acid, 3,5-bis(trifluoromethyl)phenyl phosphonic acid and phenyl phosphonic acid were then analyzed by SEC in THF (**Figure 11**). In the latter case, several concentrations were tested. Oligomers with increasing mass should be formed from the hydrolysis of 1 NCO group to an amine function and the subsequent addition of this amine on another isocyanate. The first steps of this reaction are shown in **Scheme 5**, and indeed these molecules and analogous higher

oligomers can presumably be associated with the distinctive peaks (elution volumes: 20.32, 20.81, 21.51 and 22.56 mL, respectively) detected in the chromatograms. One could even imagine the formation of the uretdione dimer of IPDI ($M = 444$, See **Scheme S2** in **supporting information**). As the catalyst concentration increases, oligomers with increasing molar masses are formed, whereas decreasing amounts of unreacted IPDI are present, consistently with an increasingly fast hydrolysis of the IPDI molecules. In the same way, when used at 1 mol%, phenyl and 3,5-bis(trifluoromethyl)phenyl phosphonic acid (“CF₃ phenyl”) lead to very similar chromatograms with the same relative amount of residual IPDI, whereas oligomers with slightly lower molar masses and higher amounts of residual IPDI are detected for 1 mol% of perfluorophenyl phosphonic acid. From this point of view, this catalyst might therefore be the most interesting, since it does not seem to promote IPDI hydrolysis as much as the others. However the side reactions observed during the prepolymer synthesis at 80 °C should be kept in mind, and additional analyses were performed on some of them.

[Figure 11 near here]

[Scheme 5 near here]

Analysis of the side reactions during prepolymer synthesis

As abnormally high NCO conversions were sometimes obtained for the prepolymer synthesis and especially in the presence of perfluorophenyl phosphonic acid, size exclusion chromatography as well as FTIR and ¹³C NMR spectroscopies were performed on the reaction product recovered at 80 °C using 1 mol% of C₆F₅P(O)(OH)₂. In FTIR, the carbonyl elongation peak was considered but all the prepolymers displayed very similar peaks with a maximum at 1716-1717 cm⁻¹. However, comparison of prepolymer prepared with the fluorinated catalyst (final $x_{\text{NCO}} = 0.78$) with another one displaying a low final NCO conversion (mesityl phosphinic acid, final $x_{\text{NCO}} = 0.25$) reveals the presence of a shoulder around 1690-1700 cm⁻¹ in the first case (see **Figure S4** in **supporting info**). This could be associated to urea or isocyanurate groups in this prepolymer.

The ¹³C NMR spectrum of this highly converted prepolymer was recorded rapidly after synthesis (**Figure 12**). Quite surprisingly this spectrum appears very simple, since only 3 signals, between 121.7 and 122.8 associated with the isocyanate functions were observed (residual IPDI and terminal groups).[45] Three other well defined peaks corresponding to the various urethane groups appear clearly at 155.4, 156.4 and 156.6 ppm.[46,47] Therefore only

2 unassigned peaks remain at 134.9 and 116.7 ppm, but they cannot be associated with allophanate or biuret (expected around 155 ppm) nor isocyanurate (expected between 150 and 153 ppm) [48,49] or between 157 and 159 ppm [50]. They do not correspond to urea carbonyls either (generally found between 158 and 160 ppm),[46] nor uretdione (156.5, 157.3 and 158.1 ppm),[51] and finally they do not belong to the catalyst.

[Figure 12 near here]

Finally the SEC chromatograms of these prepolymers (recorded after several weeks at room temperature) were carefully analyzed. High molar masses are detected in the case of perfluorophenyl phosphonic acid. A special attention was also paid to the low-molar mass species detected between IPDI (24.85 mL) and the first great peak associated with the bis(IPDI)-terminated PPG-2000 macromolecule (18.14 mL, see **Figures S3** and **S5, supporting information**). Three small peaks can be detected in this elution volume range, but they are not always present. The 1st 2 peaks (21.50 and 22.56 mL) seem to be the same as those detected during the reaction of IPDI with water (see above and **Figure 11**) and could thus correspond to a partial hydrolysis of the diisocyanate molecules.

- The 22.56 mL peak is especially high for mesityl phosphonic acid (**Fig. S5**) and also clearly visible for triflic and mesityl phosphonic acids
- The 21.50 mL peak is clearly detected only for mesityl phosphonic and perfluorophenyl phosphonic acids

Finally a 3rd peak at 22.90 mL is always present, with a rather constant but modest height. In fact, taking a closer look at **Figure 11**, the species associated with this 22.90 mL peak may also be present in IPDI / water reactions, since the 22.56 mL peaks all display a shoulder on their right side. However the concentrations are not comparable, except for the product obtained with 10 mol% of phenyl phosphonic acid. Starting from the lower molar mass side of the chromatograms, a plausible assignment would therefore associate 22.90 mL with low amounts of the uretdione dimer; its close neighbor 22.56 mL with the urea dimer (see Scheme 5); and finally 21.50 mL with a trimer. This trimer would be rather of the biuret type, since no isocyanurate could be detected in the ¹³C NMR spectrum. The uretdione dimer, or even the biuret trimer could possibly be more or less superimposed with the urethanes in the ¹³C NMR spectrum; and indeed small peaks that could be associated with this molecule appear on the left basis ($\delta \sim 155.7$ ppm) of the urethane peak at 155.4 ppm (**Figure 12**). However this interpretation remains hypothetical and other techniques such as preparative chromatography would be needed to confirm it.

To conclude on these side products, it can be assumed that at 80 °C the acidic catalysts notably enhance the isocyanate-alcohol addition kinetics, but at the same time trigger the formation of branched side products such as allophanates or biurets leading to an increase conversion NCO-groups, and to an increasing viscosity of the final product. Moreover as time goes by, the presence of catalytic species in the prepolymers also favors the hydrolysis of some isocyanate functions during storage at room temperature, leading to additional urea-type by products.

Conclusion

In order to discover new organocatalysts that could be interesting and safer alternatives to toxic tin and mercury derivatives that are widely used for polyurethane synthesis, various nucleophilic/basic or acidic organic compounds were screened in the polyaddition of a “low-reactive polyurethane system” (aliphatic dissymmetric diisocyanate / macrodiol bearing secondary hydroxyl groups) at medium and low temperature. It was found that guanidines can be interesting since they display a medium catalytic activity, but only at high enough temperature. The catalytic efficiency of these compounds seems to be related to their nucleophilicity, instead of their basicity. However, these catalysts also favor the reaction of isocyanate groups with water to a too high extent, which is a negative point.

In comparison, strongly acidic compounds such as phenyl phosphonic acid derivatives show an enhanced catalytic activity and a better water/alcohol selectivity. In this series the efficiency of the catalyst is often related to its acidity. Even though some side reactions were observed at high temperature, these derivatives and especially perfluorophenyl phosphonic acid can be seen as really promising new environmentally friendly catalysts, even for challenging polyurethane materials such as transparent elastomers prepared by the casting of low-reactivity precursors at room temperature.

Acknowledgements

This work was funded by the French FUI (Fond Unique Interministériel), under the aegis of Techtera Competitvity Pole, as the Collaborative Project “ECOMAT” (Ecomatériaux souples [Textile et Papier fonctionnalisés]). We gratefully acknowledge all the partners from the ECOMAT Project for fruitful discussions. Special thanks are addressed to Juxta-Allrim (especially Dominique Benazet and Guy Rosier), also for providing several catalysts and

reagents. We also thank the NMR Polymer Center of the “Institut de Chimie de Lyon” (FR3023), for assistance and access to the NMR facilities. We thank Dr Nguyen Viet-Hoang for the preparation of one catalyst.

This paper is dedicated to the memory of our colleague and friend Laurent Saint-Jalmes (Bluestar Silicones France), who managed the whole ECOMAT project with remarkable efficiency, skill and warmth.

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Figure captions

Figure 1. Kinetics of the reaction between IPDI and PPG-2000 ($[\text{OH}]/[\text{NCO}] = 0.5$) at 60 °C in bulk, in the presence of 1 mol% guanidine catalyst

Figure 2. ^1H NMR spectrum (DMSO-d_6) of the reaction product of IPDI (1 eq.) with PGME (1 eq.) capped with di(n-butyl) amine (see assignments in Scheme 4)

Figure 3. ^1H NMR spectra (DMSO-d_6) of the IPDI-NCO prepolymer ($[\text{NCO}]/[\text{OH}] = 2$) synthesized at 60 °C in the presence of 1 mol% TMG, of the IPDI-PPG polymer ($[\text{NCO}]/[\text{OH}] = 1$) synthesized at 60 °C in the presence of ~32 mol% TMG, and of the pure IPDI-TMG adduct

Figure 4. Kinetics of the reaction between IPDI and PPG-2000 ($[\text{OH}]/[\text{NCO}] = 0.5$) at 60 °C in bulk, in the presence of TMG or IPDI-TMG adduct as catalyst

Figure 5. Kinetics of the reaction between IPDI and PPG-2000 ($[\text{OH}]/[\text{NCO}] = 0.5$) at 80 °C in bulk, in the presence of 1 mol% guanidine derivative as catalyst; the case of DBTDL (0.0056 mol%) was added for comparison

Figure 6. Kinetics of the reaction between IPDI and PPG-2000 ($[\text{OH}]/[\text{NCO}] = 0.5$) at 80 °C in bulk, in the presence of 1 mol% acidic derivative as catalyst; the case of DBTDL (0.0056 mol%) was added for comparison

Figure 7. Kinetics of the reaction between IPDI and PPG-2000 ($[\text{OH}]/[\text{NCO}] = 0.5$) at 80 °C in bulk, in the presence of increasing amounts of phenyl phosphonic acid as catalyst; comparison with DBTDL (0.0056 mol%)

Figure 8. Effect of the temperature on the kinetics of the reaction between IPDI and PPG-2000 ($[\text{OH}]/[\text{NCO}] = 0.5$) catalyzed by 1 mol% phenyl phosphonic acid or 3,5-bis(trifluoromethyl)phenyl phosphonic acid (“ CF_3 phenyl”)

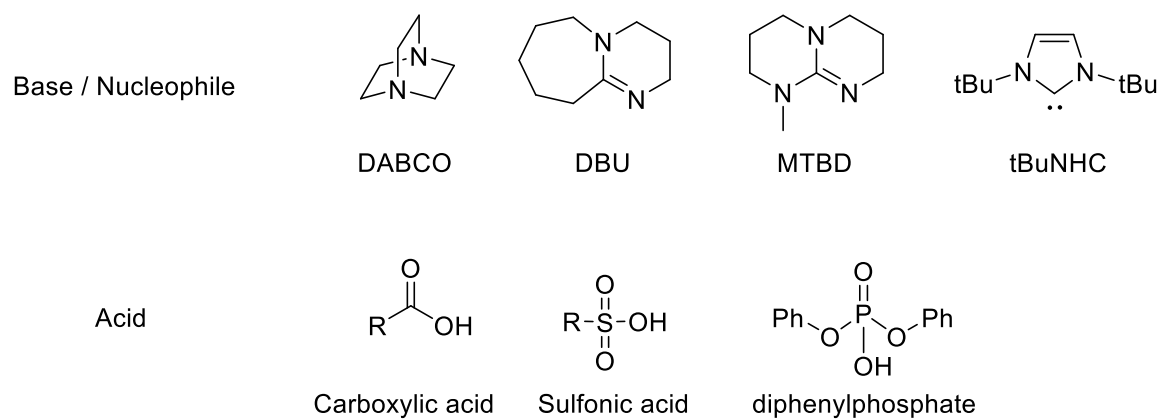
Figure 9. ^1H NMR spectra (DMSO-d_6) of the prepolymers obtained by the bulk reaction between IPDI and PPG-2000 at 80 °C ($[\text{NCO}]/[\text{OH}] = 2$) using 1 mol% catalyst

Figure 10. Kinetics of the reaction between IPDI and PPG-2000 or water at 20 °C ($[\text{NCO}]/[\text{OH}] = 2$), in the presence of increasing amounts of phenyl phosphonic acid as catalyst

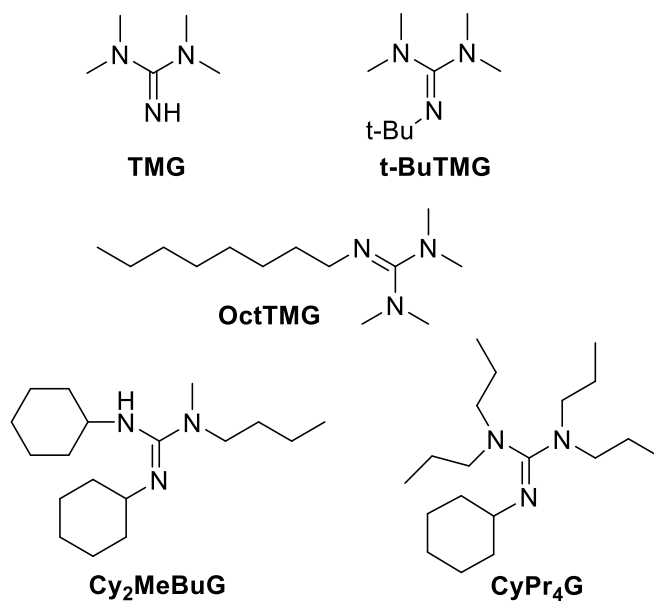
Figure 11. Size exclusion chromatography analysis of the products of the reaction between water and IPDI ($[\text{NCO}]/[\text{OH}] = 2$) in DPGDME solution at 20 °C, in the presence of various catalysts (after 3-4 weeks at room temperature)

Figure 12. ^{13}C NMR analysis (carbonyl signals, CDCl_3 , 100 MHz) of the PPG2000-IPDI prepolymer ($[\text{NCO}]/[\text{OH}] = 2$) synthesized at 80 °C in the presence of 1 mol% perfluorophenyl phosphonic acid and displaying a final conversion $x_{\text{NCO}} = 0.78$

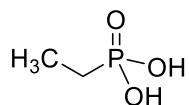
Scheme 1. Selection of Basic/Nucleophilic and Acidic organocatalysts reported for PUs preparation.



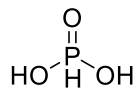
Scheme 2. Different guanidine catalysts used in this work



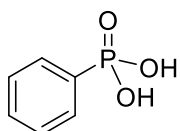
Scheme 3. Different phosphorus based acidic catalysts used in this work



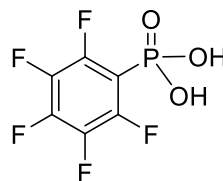
Ethyl phosphonic acid



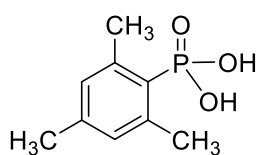
Phosphonic acid



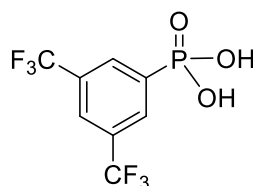
Phenyl phosphonic acid



Perfluorophenyl phosphonic acid

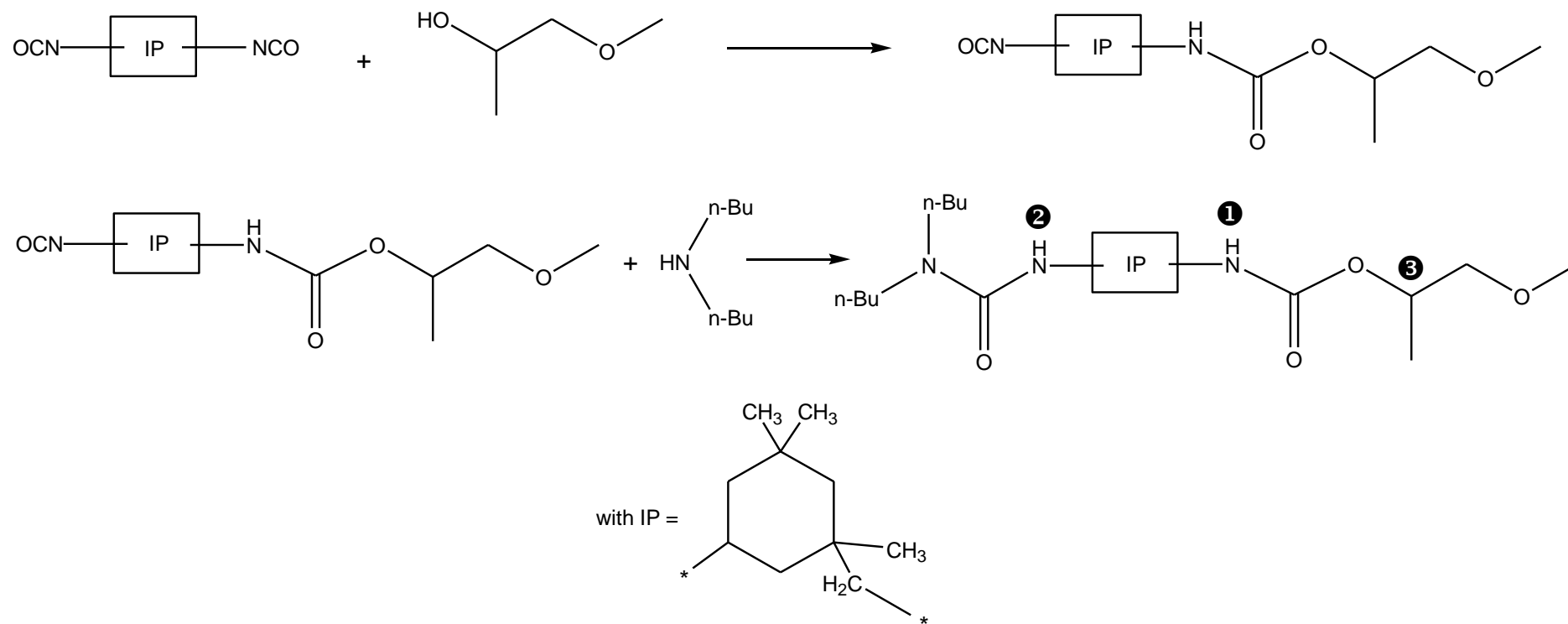


Mesityl phosphonic acid

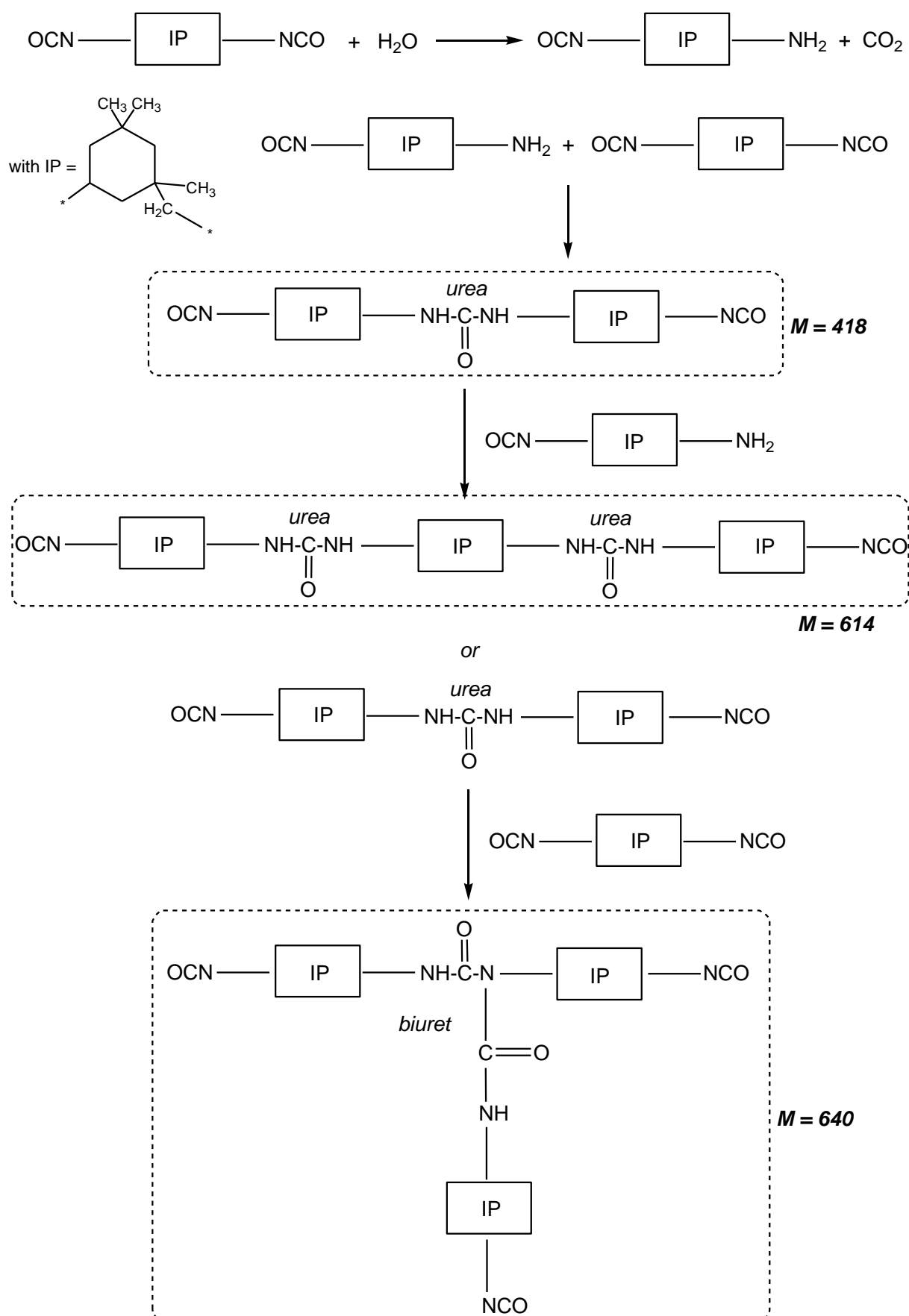


3,5-bis(trifluoromethyl)phenyl phosphonic acid

Scheme 4. Reaction between IPDI and PGME, and subsequent capping of the residual NCO groups using di(n-butyl) amine



Scheme 5. First stages of the reaction between IPDI and water



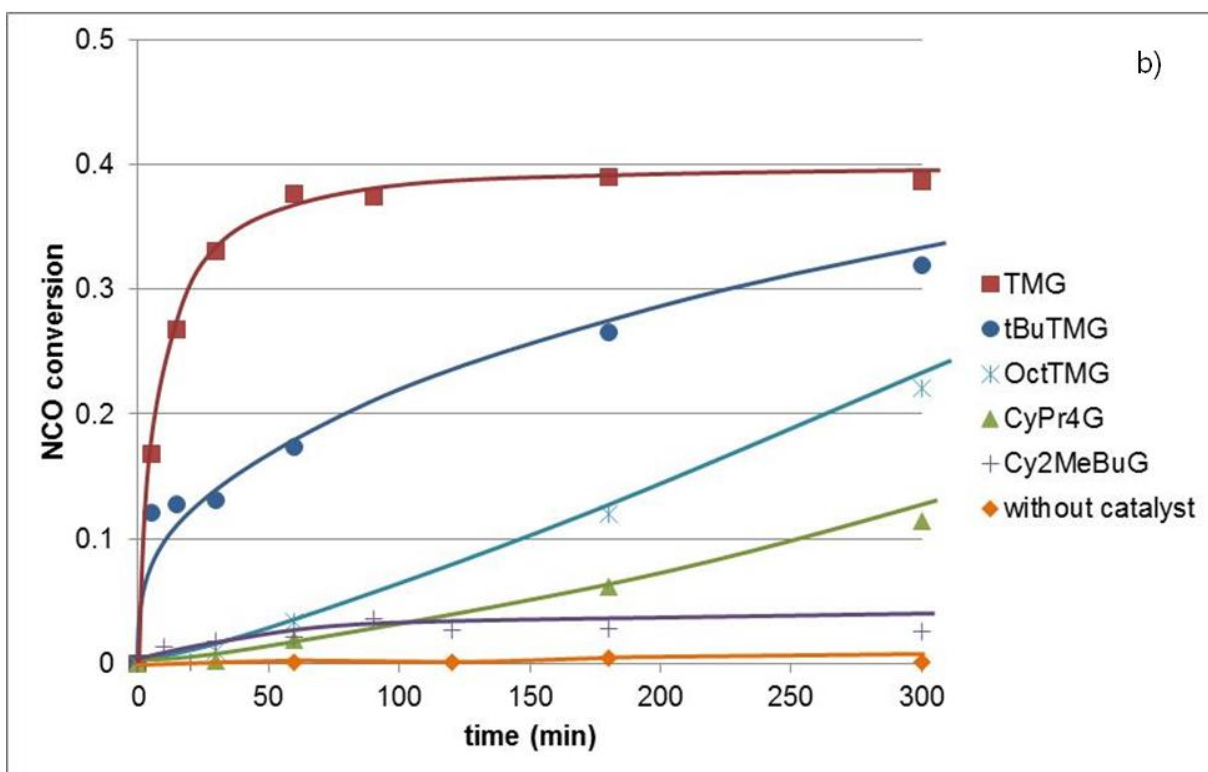
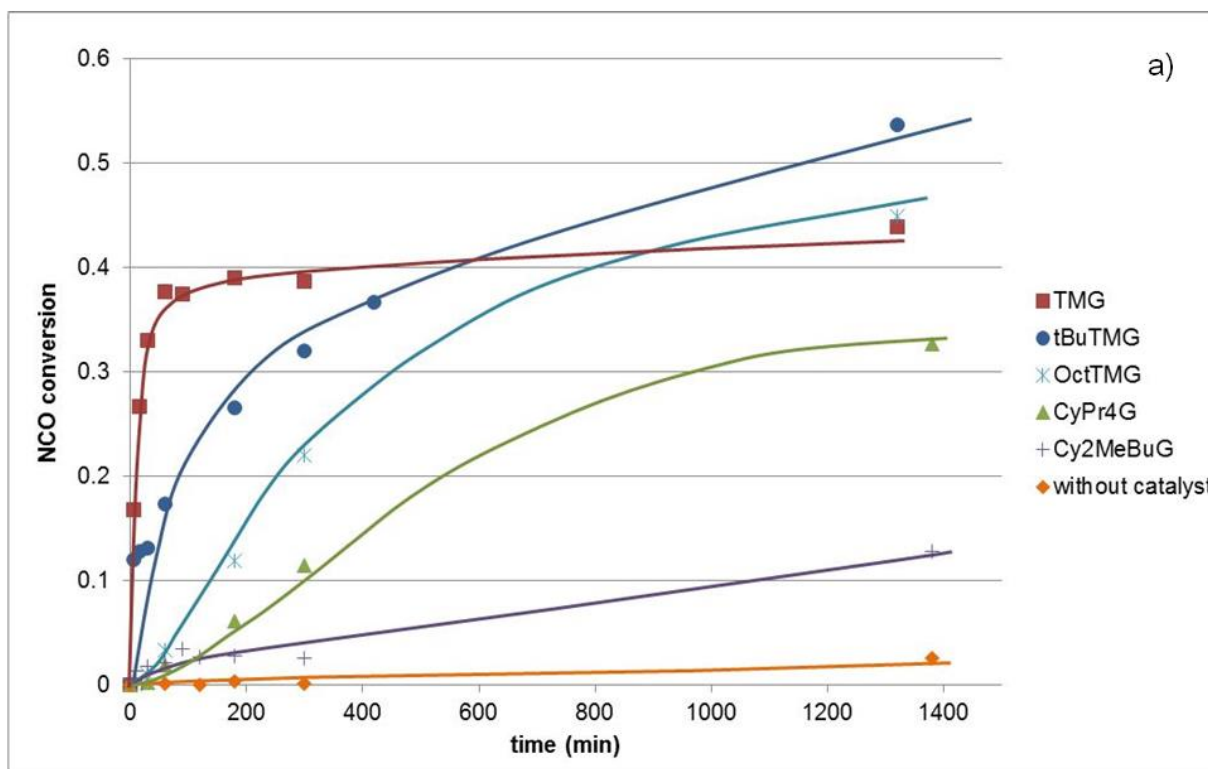


Figure 1. Kinetics of the reaction between IPDI and PPG-2000 ($[OH]/[NCO] = 0.5$) at 60 °C in bulk, in the presence of 1 mol% guanidine catalyst

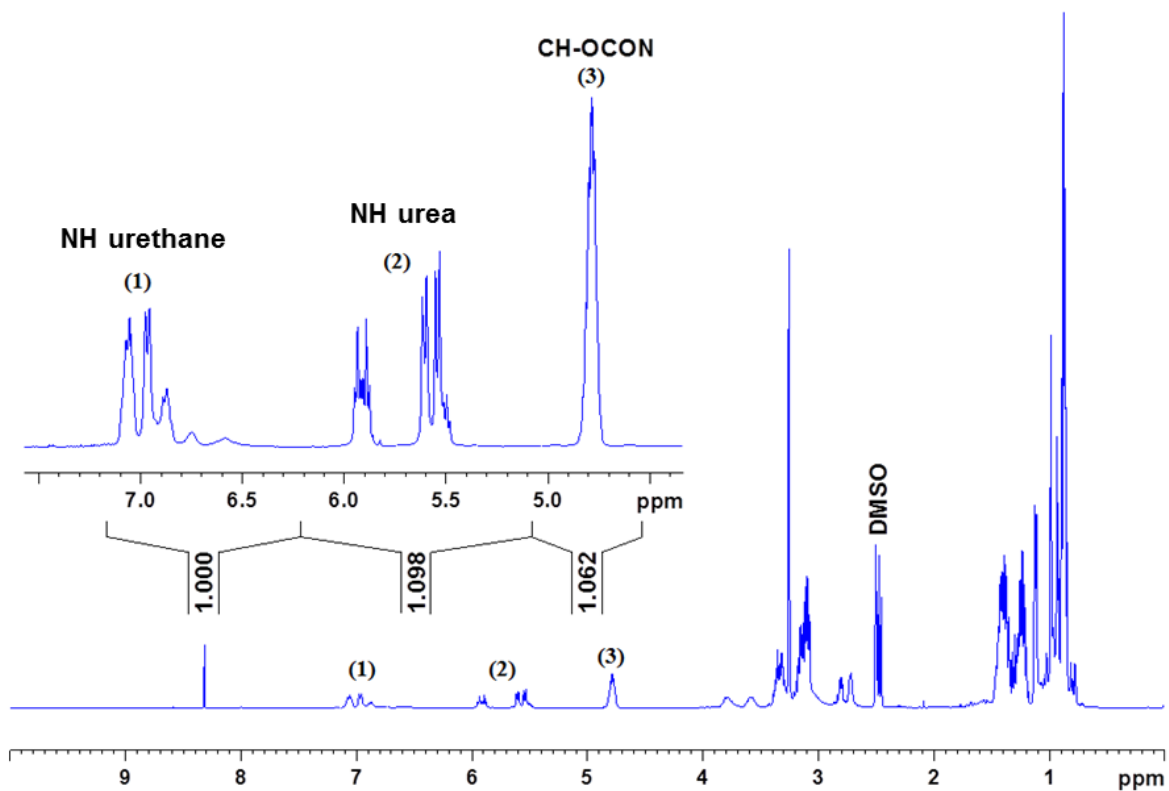


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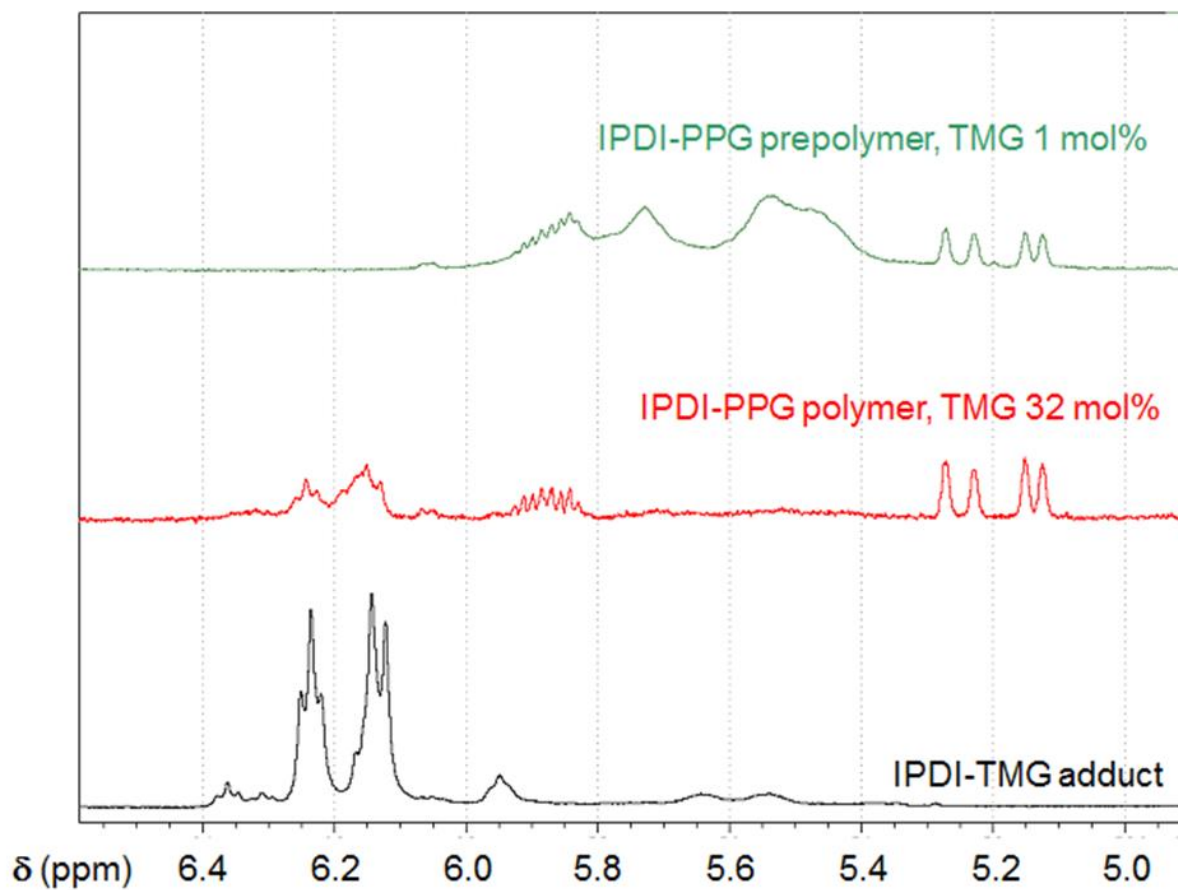


Figure 3. ¹H NMR spectra (DMSO-d₆) of the IPDI-NCO prepolymer ([NCO]/[OH] = 2) synthesized at 60 °C in the presence of 1 mol% TMG, of the IPDI-PPG polymer ([NCO]/[OH] = 1) synthesized at 60 °C in the presence of ~32 mol% TMG, and of the pure IPDI-TMG adduct

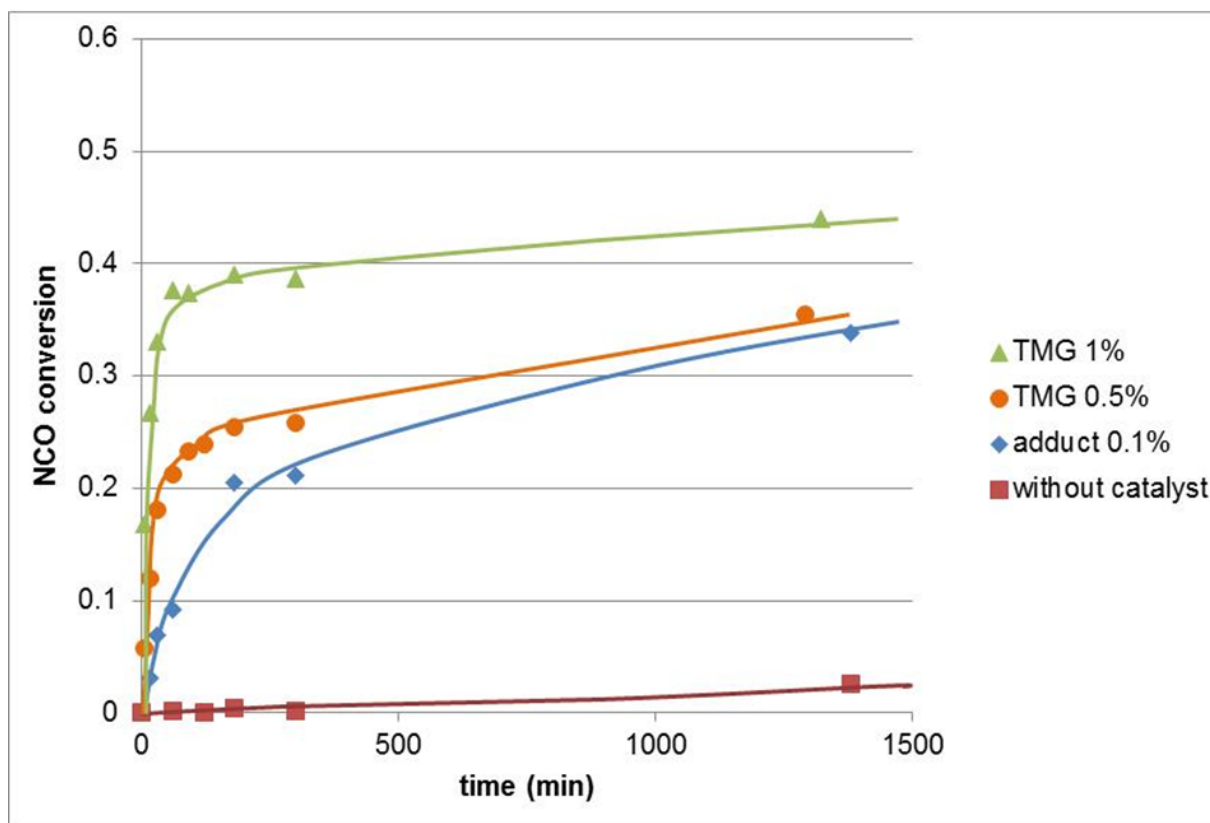


Figure 4. Kinetics of the reaction between IPDI and PPG-2000 ($[OH]/[NCO] = 0.5$) at 60 °C in bulk, in the presence of TMG or IPDI-TMG adduct as catalyst

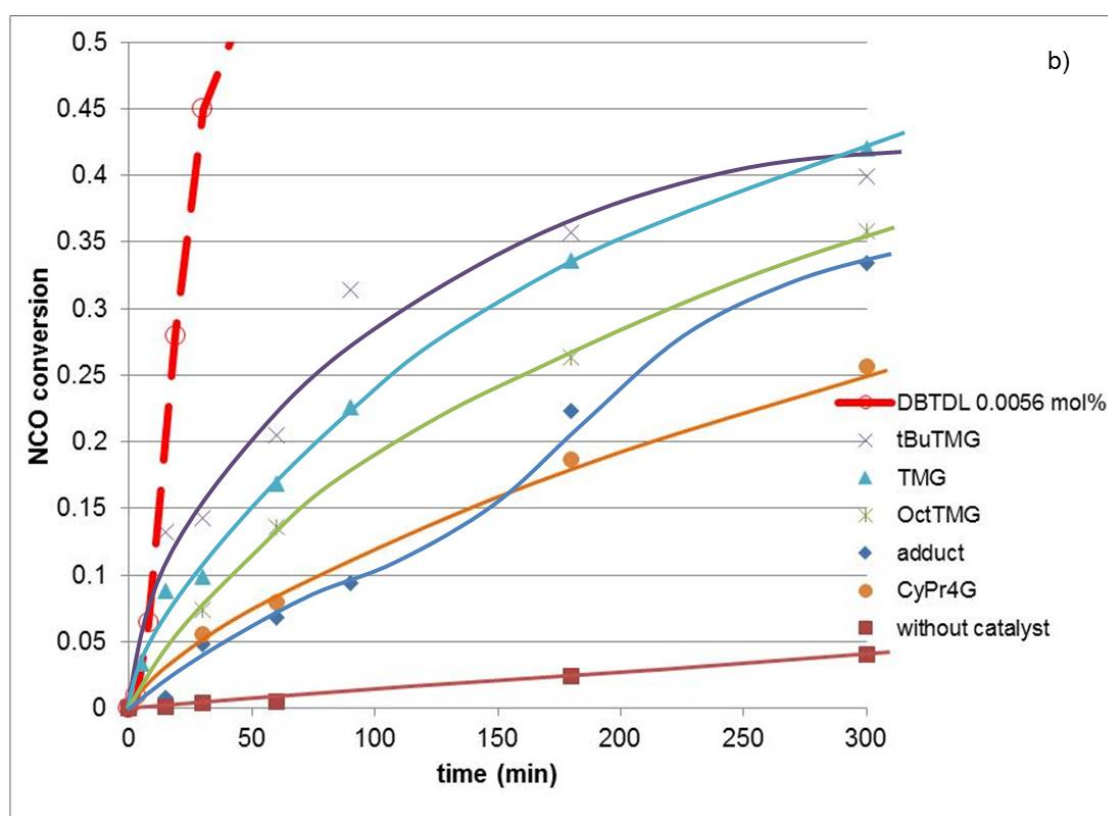
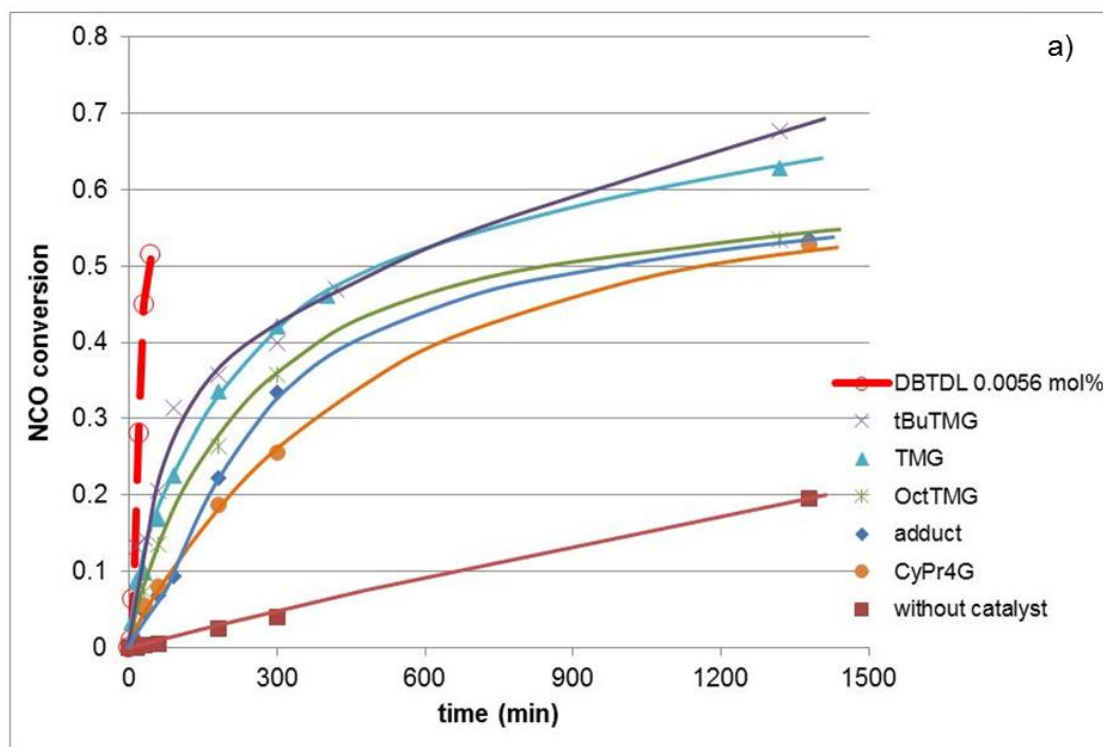


Figure 5. Kinetics of the reaction between IPDI and PPG-2000 ($[OH]/[NCO] = 0.5$) at 80 °C in bulk, in the presence of 1 mol% guanidine derivative as catalyst; the case of DBTDL (0.0056 mol%) was added for comparison

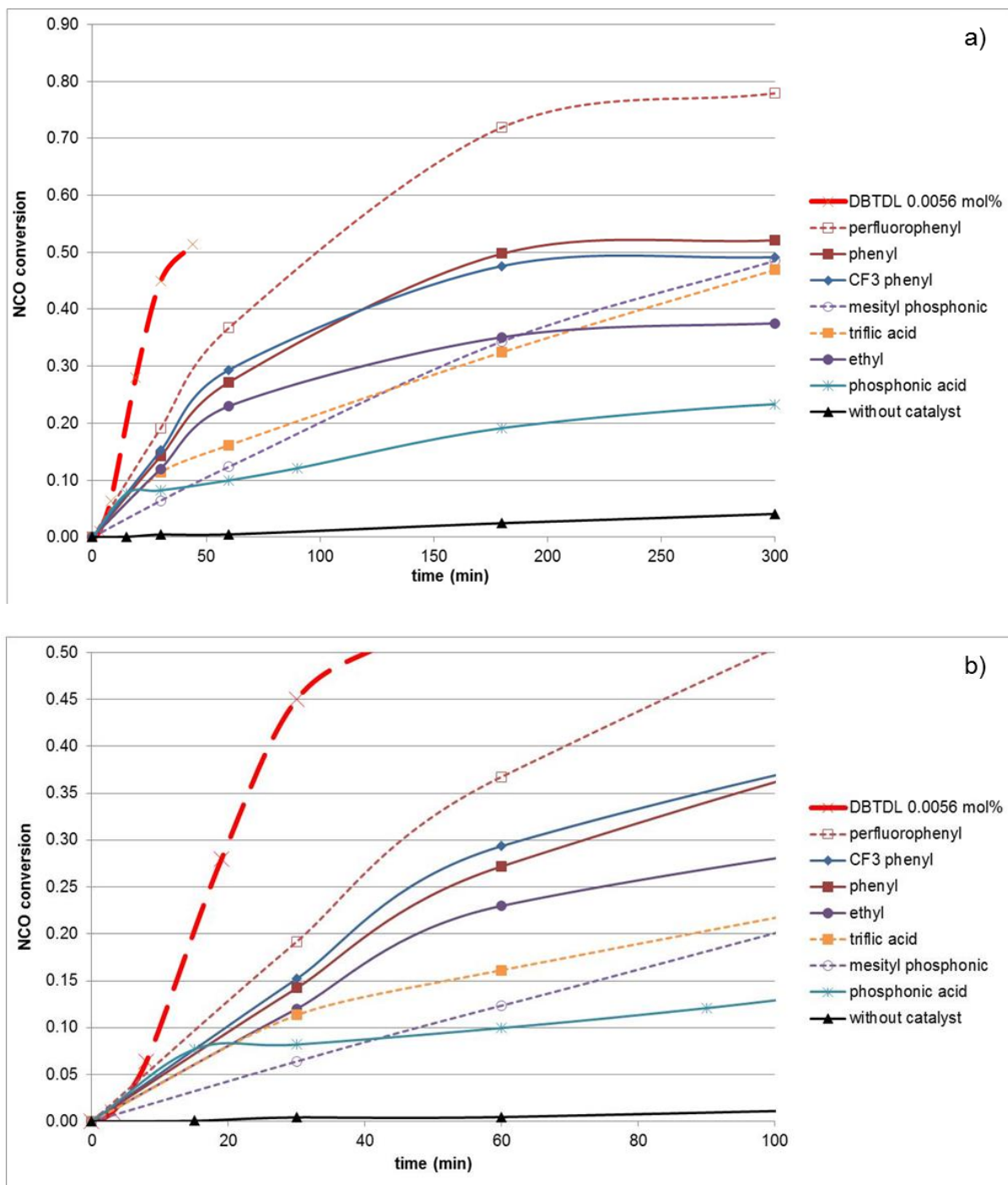


Figure 6. Kinetics of the reaction between IPDI and PPG-2000 ($[OH]/[NCO] = 0.5$) at 80 °C in bulk, in the presence of 1 mol% acidic derivative as catalyst; the case of DBTDL (0.0056 mol%) was added for comparison

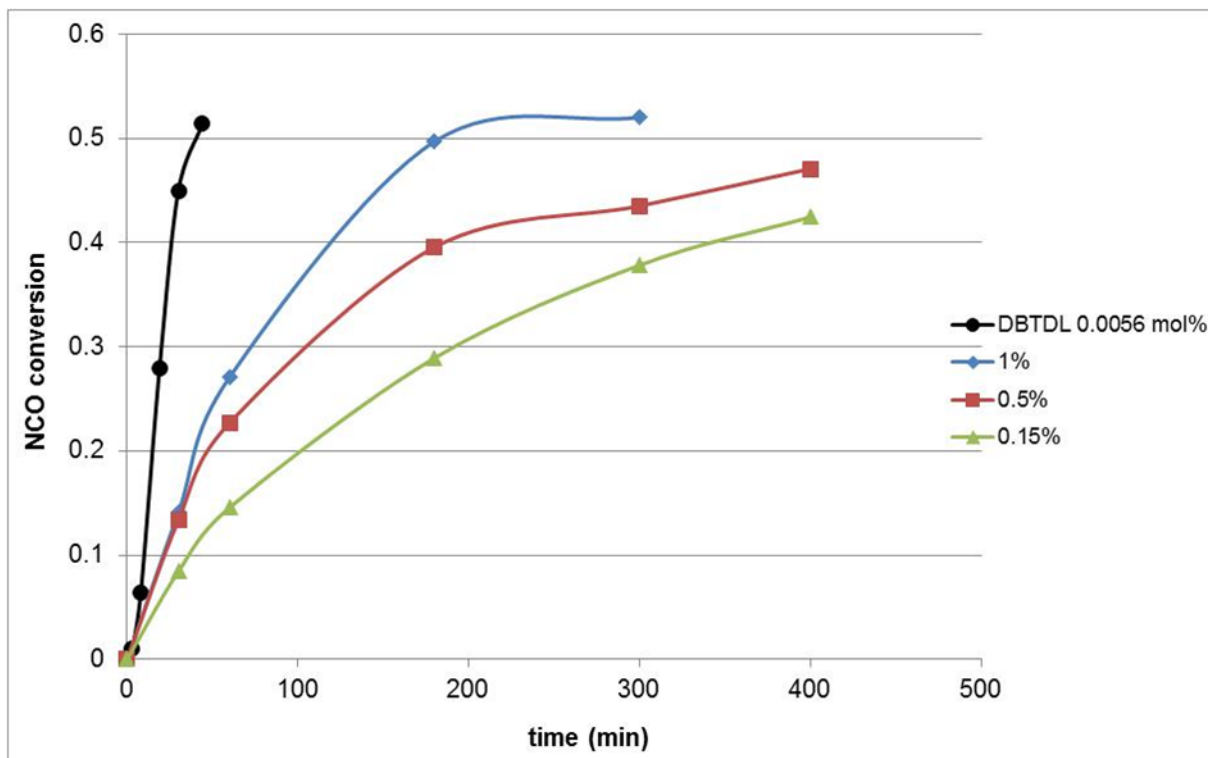


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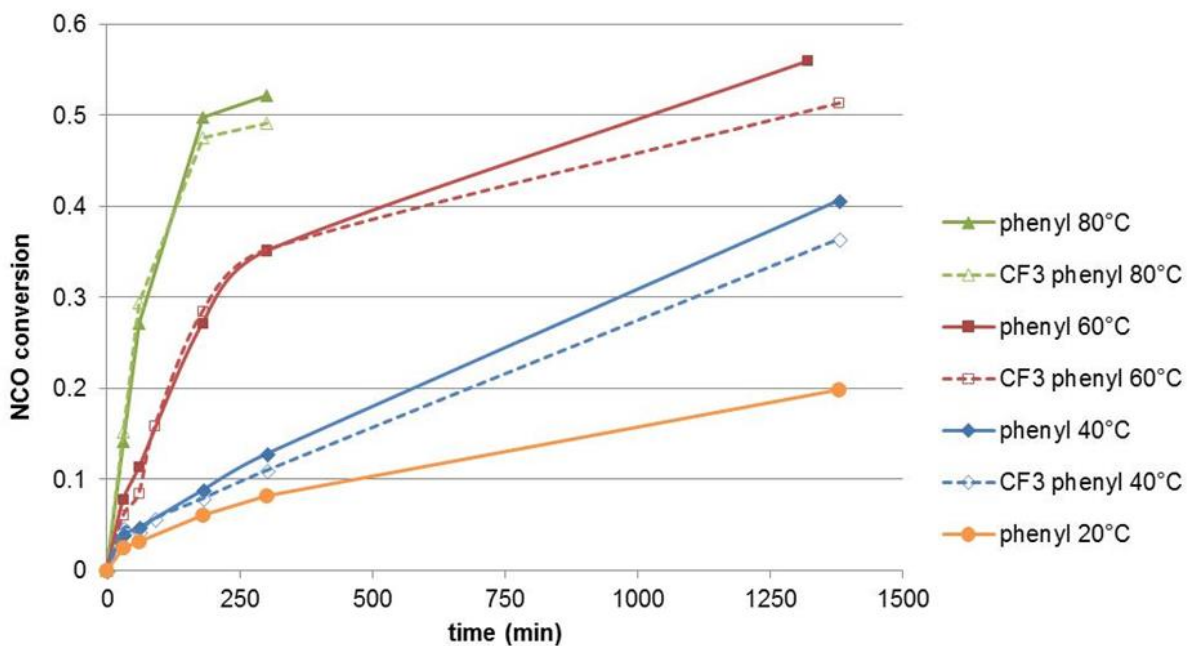


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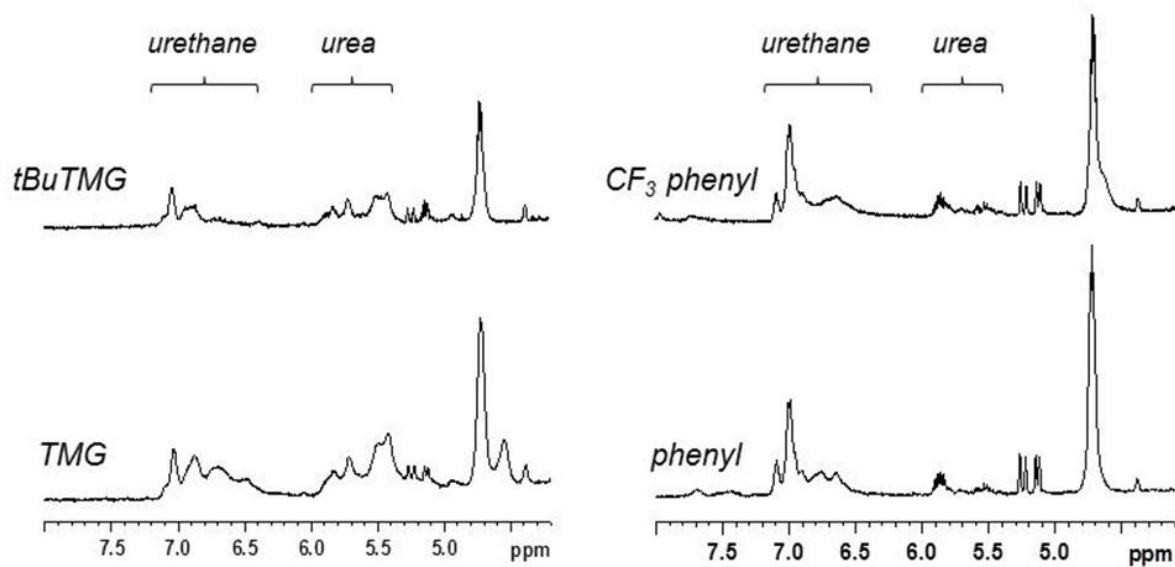


Figure 9. ¹H NMR spectra (DMSO-d₆) of the prepolymers obtained by the bulk reaction between IPDI and PPG-2000 at 80 °C ([NCO]/[OH] = 2) using 1 mol% catalyst

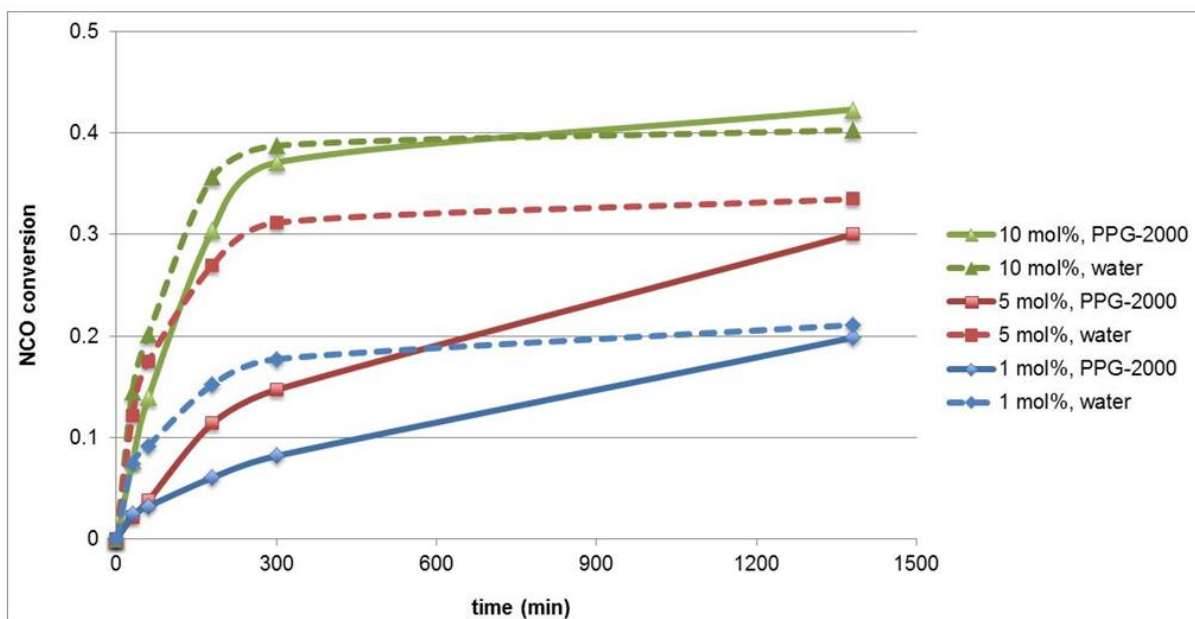


Figure 10. Kinetics of the reaction between IPDI and PPG-2000 or water at 20 °C ($[NCO]/[OH] = 2$), in the presence of increasing amounts of phenyl phosphonic acid as catalyst

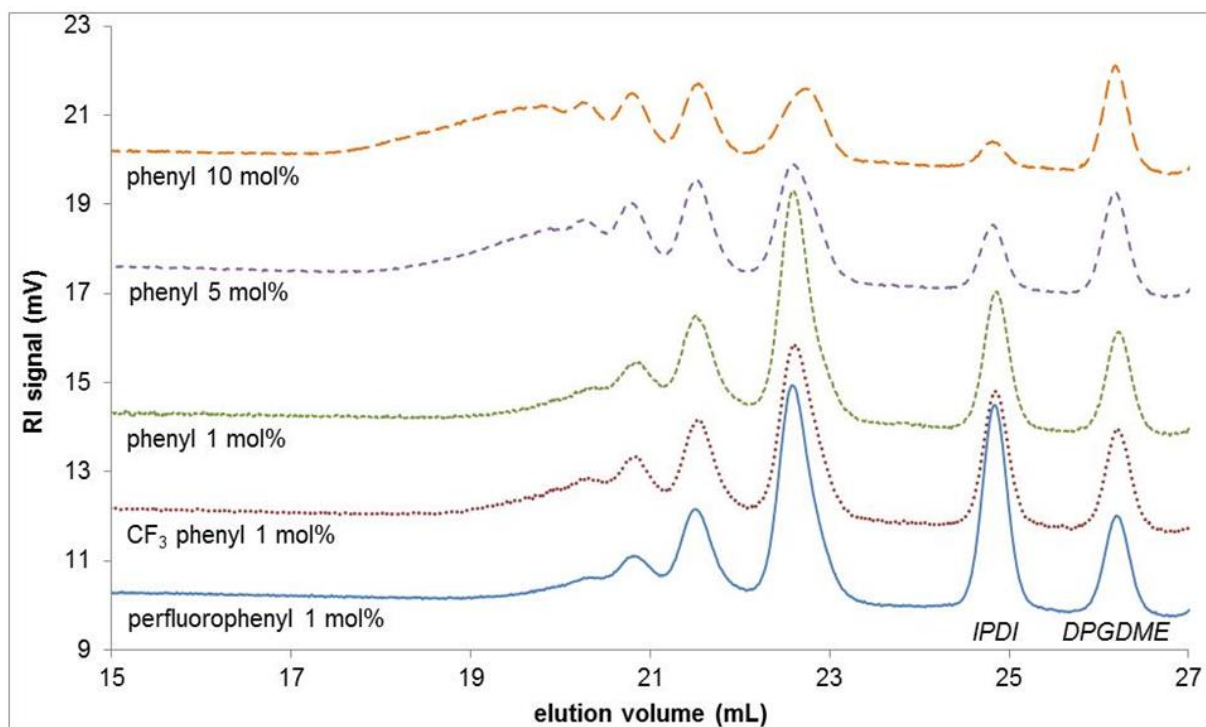


Figure 11. Size exclusion chromatography analysis of the products of the reaction between water and IPDI ($[NCO]/[OH] = 2$) in DPGDME solution at 20 °C, in the presence of various catalysts (after 3-4 weeks at room temperature)

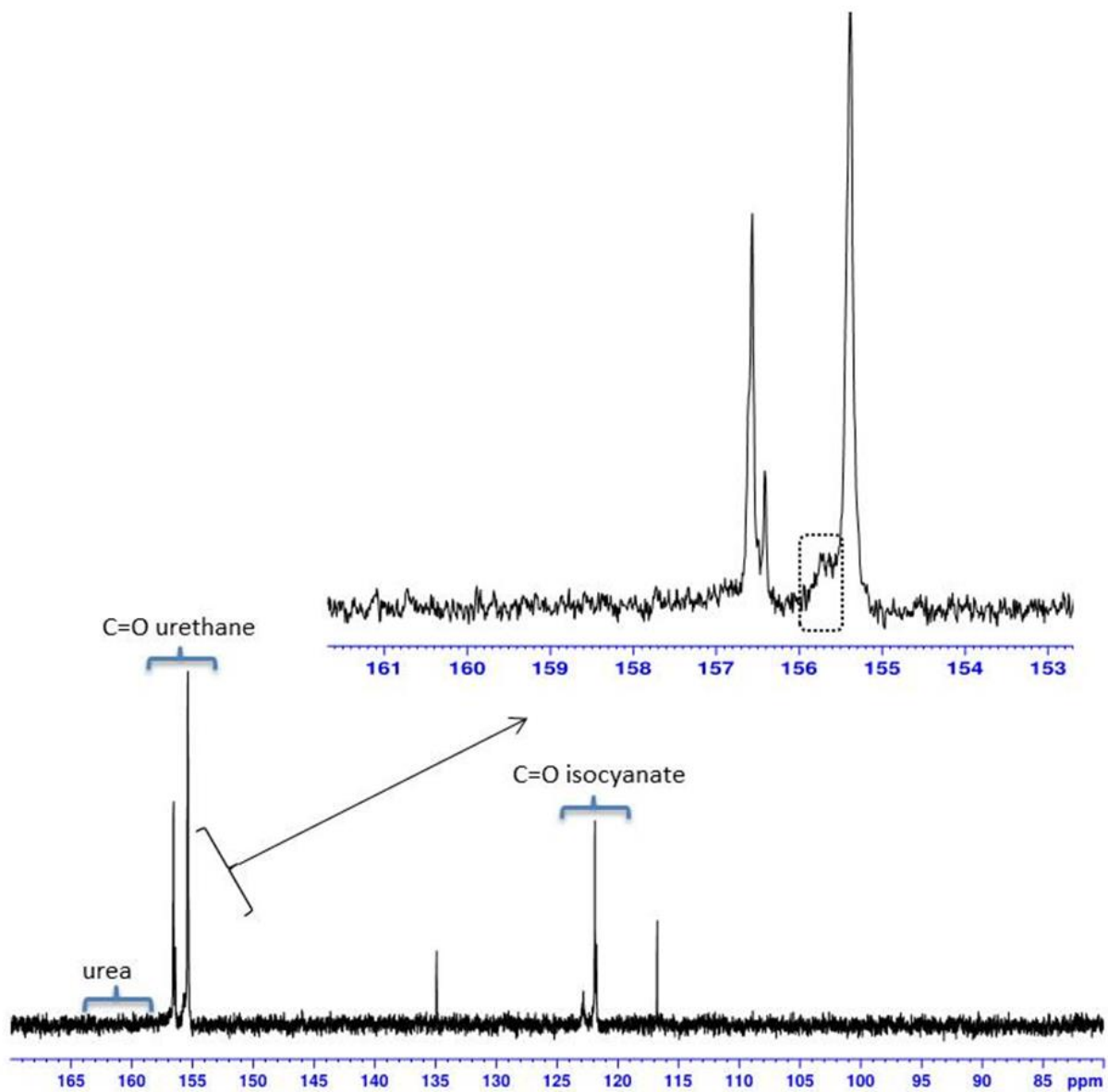


Figure 12. ^{13}C NMR analysis (carbonyl signals, CDCl_3 , 100 MHz) of the PPG2000-IPDI prepolymer ($[\text{NCO}]/[\text{OH}] = 2$) synthesized at 80 °C in the presence of 1 mol% perfluorophenyl phosphonic acid and displaying a final conversion $x_{\text{NCO}} = 0.78$