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Urea and polyurea production: an innovative solvent and catalyst free approach through catechol carbonate.

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Catechol carbonate, substituted urea, polyurea, aminolysis, solvent free, catalyst free.

ABSTRACT

The peculiar reactivity of catechol carbonate (CC) with amines and polyamines in both solvent and catalyst free conditions is herein described. In all the tests performed at room temperature, CC conversion reached 100% in few seconds leading to the selective formation of the corresponding 2-hydroxyphenylcarbamate. This compound is further rapidly converted to the di-substituted urea by the consecutive nucleophilic attack of another amine. Noteworthy, the application of this approach can be successfully extended to the one-pot bio-amine based synthesis of polyurea as herein proposed for the first time in literature. The reaction is of general purpose for primary amines and catechol can be easily recovered by sublimation as pure crystals ready to be recycled for the synthesis of new CC. An exception is related to the reactivity of secondary amine, which leads anyway to the selective formation of substituted phenolic carbamates (e.g. 2-hydroxyphenyl diethylcarbamate), suitable as intermediates in medicinal chemistry.

Introduction

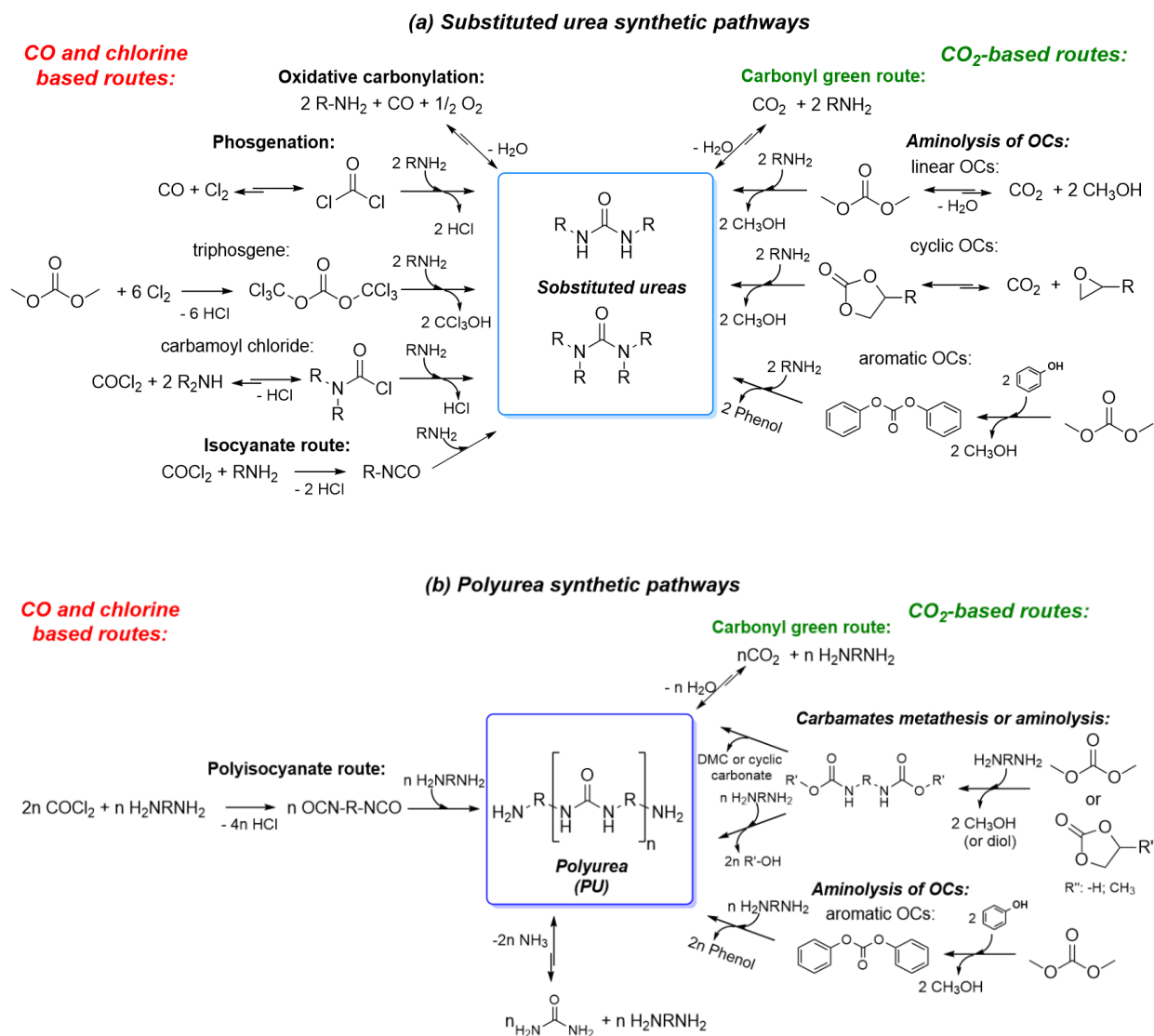
Substituted urea can be exploited in a wide range of applications: as antioxidants in gasoline,¹ agricultural chemicals,²⁻⁴ dyes and intermediates,⁵⁻⁸ additives in polymers synthesis,⁹ or thanks to their useful biological activities as structural components for drugs, HIV protease inhibitors, heme-regulated inhibitor kinase (HRI), CCK-B receptor and endothelin antagonists, to name a few.¹⁰⁻¹⁸ Moreover, their structures represent the skeleton of polymeric materials such as polyurea (PU).¹⁹ Although PU have been known for years in industry for their peculiar properties and high performance,²⁰ huge efforts have been done in order to find new applications for these compounds. As a matter of fact, in the very last years, several papers have been published, proposing new potential applications in the fields of special coatings,^{21,22} innovative elastomers,²³ protective

agents against dynamic loads, like blast and ballistics²¹, and for the production of special composite materials with unique properties,^{24,25} just to name a few. As a general trend, PU are characterized by high chemical, thermal and mechanical stabilities, in this way showing better physical properties compared to their polyurethane counterpart.²⁶ Moreover, PU can be spun into fibers or postprocessed in order to obtain films with great potentials in the food preservation and medical applications.²⁷

Interestingly, in the last years the availability of different bio-based amines have opened new perspectives for the synthesis of bio-PU.^{28,29} In particular, 1,4-butandiamine and 1,5-pentandiamine can be derived from lysine and ornithine, respectively, through decarboxylation, whereas hexamethylenediamine can be obtained by fermentation with engineered yeasts developed by Genomatica.³⁰

Different synthetic strategies can lead to the formation of both urea and polyurea. In particular, similar carbonylating agents can be used for the synthesis of both low and high molecular weight products (Scheme 1). Unfortunately, the traditional (and most used) carbonylating agents are hazardous and toxic compounds, namely phosgene (or its safer analogue triphosgene),³¹ and CO further requires harsh and dangerous reaction conditions and a Pd-based catalyst.³²⁻³⁶ Other explored approaches use carbamoyl chloride (for monomeric urea) or isocyanate as reactants, both produced from phosgene as well.^{37,38} Although some improvements have been reported regarding the manufacturing process of isocyanates,^{39,40} the need for a large excess of phosgene, the formation of stoichiometric HCl as a co-product and the great dilution of the reagents are still problems to be solved.⁴¹⁻⁴³ Recently, the synthesis of substituted urea through the aminolysis of inorganic cyanate (KOCN) in water has also been proposed.⁴⁴ However, these approaches are neither environmentally-friendly nor safe, leading also to the production of important amount of

inorganic wastes. Indeed, in order to overcome the notorious toxicity of isocyanates new alternative and efficient routes are needed.^{45,46}



Scheme 1. Traditional synthetic routes to both urea (Scheme 1, a) and polyurea (Scheme 1, b). Scheme 1, a: “CO and chlorine based routes”, oxidative carbonylation³²⁻³⁶, phosgenation,³¹ use of triphosgene³¹ or carbamoyl chloride,³⁸ isocyanate route.³⁷ “CO₂ based routes”: condensation of CO₂ and amines,^{49,56} aminolysis of linear aliphatic,^{70,71} cyclic aliphatic^{72,73} and linear aromatic organic carbonates.⁷⁶

Scheme 1, b: “CO and chlorine based routes”, polyisocyanate route.^{37,39,40} “CO₂ based routes”: condensation of CO₂ and polyamines,^{24,27,50-57} carbamate metathesis or aminolysis,⁵⁸⁻⁶³ aminolysis of both linear aromatic carbonates⁷⁸ and inorganic urea.^{47,48}

The main non-isocyanate routes (NIR) are based on the utilisation of CO₂ (the so-called “carbonyl green route”) and its derivatives, including inorganic urea.^{47,48} Although the reaction yields water as the only co-product, it requires a suitable solvent and harsh reaction conditions to overcome the strictly thermodynamic limitations.^{24,49} Noteworthy, recent publications devoted to the polycondensation of CO₂ with diamines toward oligoureas are only a few and still maintain difficult operating conditions, a bottleneck for the application at industrial level.^{27,50-57}

On the other hand, interesting results in PU synthesis have been achieved by the strong bases catalysed polycondensation of CO₂ derivatives, namely organic carbamates, with diamine.^{20,58-63}

Although organic carbamates can be achieved by the condensation reaction of amines, CO₂ and alcohols, the main applied synthetic procedure is through the aminolysis of organic carbonates (OCs).⁶⁴⁻⁶⁶ Therefore, a step forward for both atom economy and process simplification is the direct synthesis of PU from OCs such as linear (dimethyl, DMC) and cyclic (ethylene and propylene) aliphatic carbonates or linear aromatic carbonate (diphenyl carbonate, DPC).⁶⁷⁻⁷³

Although greener, the last approaches, show some drawbacks for industrial applications. First of all, OCs generally shows lower reactivity if compared to isocyanates;^{74,75} then, the use of both solvents (e.g. tetramethylenesulfone or toluene) and, in most of the cases, of homogenous catalytic bases (e.g. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU), 2-hydroxypyridine and potassium methoxide or tert-butoxide) cannot be avoided.^{58,59,64-66,74-77} In this way, we could meet difficulty in handling, recover and reuse the catalytic system

and lastly we cannot avoid relatively high reaction temperatures. Anyway promising results in terms of urea yields⁷⁸⁻⁸⁰ pave the way for a further improvement of several parameters, such as solvent less and catalyst free conditions, lowering of reaction temperature, easy purification and recovery of recyclable co-products, before extending this procedure to a successful application in polymer (PU) production.

With this aim in mind, we explored the literature finding only two examples reporting on the reactivity of cyclic aromatic carbonates with amines. 4-propylcatechol carbonate was employed as a carbonylating agent in a Lewis acid catalyzed two-step production of carbamates, with long reaction time and in 2-methyl-THF as solvent,⁸¹ while a nitro substituted catechol is employed in the synthesis of ureas with quite long reaction time.⁸²

Starting from this state of the art and considering our experience in the synthesis and reactivity study of cyclic organic carbonates with alcohols,⁸³⁻⁸⁶ we are here proposing catechol carbonate (CC, Figure 1) as a promising candidate for the development of a new synthetic pathway for the preparation of PU, the latter never obtained from aromatic cyclic carbonates.

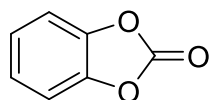


Figure 1. Catechol carbonate (CC) structure.

In particular, the fine-tuning of the reaction between catechol carbonate (CC) and substituted amines, demonstrated the possibility to exploit the high reactivity of CC for a low temperature, high yielded, solvent and catalyst free synthesis of urea. Once obtained suitable reaction conditions for the synthesis, co-product recover and recycling for monomeric urea, the system has been adapted and scaled-up to the multi-grams production of PU. In particular, the polycondensation of CC with diamines such as 1,4-butandiamine, 1,5-pentandiamine and 1,6-hexamethylenediamine

which are known as bio-based building blocks, have been investigated leading to the innovative isocyanate-free one-pot synthesis of polyurea (PU).

Experimental section

Materials

Reagents and solvents have been supplied by Sigma Aldrich and used without further purifications.

CC was prepared by the carbonate interchange reaction of DMC and catechol, using a reactive distillation apparatus optimised as reported by the same authors in the recent literature, obtaining an isolated yield of 90% in 24 hours of reaction.⁸³

Reaction procedure and product analysis: symmetric urea synthesis

Reactions were conducted, at room temperature, in a 2mL screw cap Pyrex glass vials equipped with a magnetic stirrer. In a typical experiment, the flask was charged with the amine (usually 1.5 mmol) then the desired amount of CC (0.15 mmol) was slowly added to the liquid phase under stirring. During this step, the exothermicity of the reaction was monitored, and in particular with the most volatile amines, controlled by cooling the mixture with an ice bath. The mixture was then stirred for 1 h and finally recovered with either acetone (2 mL, HPLC grade, Sigma-Aldrich) for the GC-MS analysis or 0,6 mL DMSO-d₆ for the NMR investigation. Most of the reactions were replicated three times to verify their reproducibility. In the repeated runs carried out under the same conditions, the values of conversion and product yields (determined by NMR) differed by less than 3% from one reaction to another. The reaction mixtures were analysed by means of a GC-MS equipped with a non-polar column HP-5 (95%dimethylsiloxane - 5% phenyl, 30 m × 320 μm, T injector: 280 °C; split ratio: 50:1, He flow: 1.0 mL min⁻¹), by using the following temperature ramp: 50 °C for 2 min, with subsequent heating at 10 °C min⁻¹ up to 280 °C (hold for

5 min). The structure of products was assigned by GC-MS and, whenever possible, by comparison with commercially available samples.

In-situ NMR experiments

Reactions were performed at room temperature for the time required without stirring. The reaction was monitored by ^1H -, ^{13}C - NMR using a Varian Inova 400 (^1H , 400; ^{13}C , 100 MHz) instrument. General procedure: 20 mg of catechol carbonate have been added into an NMR tube containing an excess (10:1 or 5:1) of amine in 0.6 mL of DMSO- d_6 . Both isopropyl and n-butyl amine were tested as reagent for the selective synthesis of the corresponding ureas.

Reaction procedure and product analysis: polyurea synthesis

Regarding the synthesis of PU a different reaction setup has been employed. In particular, in order to overcome the increasing viscosity of the reaction mixture, promoted by the polymerisation reaction carried out in the absence of solvent to contain the environmental impact, a thermostated and mechanically stirred (50 rpm) glass vial (50 ml) equipped with an ice-cooled trap was used. Besides, in the case of polymeric systems, higher amount is needed for solid-state and functional property characterization. To do so, the reagent amounts loaded inside the reaction system have been scaled up to around sixty times compared to the monomeric urea synthesis. In particular, CC and the defined diamine were charged in equal molar amount (8.8 mmol) in the reactor and mixed at room temperature under nitrogen atmosphere for 15 min. Afterwards, the silicon oil bath was set at 70°C and maintained for 45 min. Then, the temperature was increased to 110°C and maintained at this value for 90 minutes. In order to promote the proceeding of the reaction and recover the catechol developed, after 90 minutes from the beginning of the reaction, the pressure was progressively reduced to 0.5 mbar. In the last stage, the temperature was increased to 200°C and kept for 90 minutes. Then, the PU synthesized were discharge from the vial.

The chemical structure was confirmed by ^1H - and ^{13}C -NMR spectroscopy (in deuterated trifluoroacetic acid, TFA-d) together with Attenuated total reflectance-Fourier transform infrared spectroscopy (Perkin Elmer ATR-FTIR: 32 scans with 4 cm^{-1} of resolution over $450\text{-}4000\text{ cm}^{-1}$ wavelength range). ^1H -NMR analysis has also been used to calculate the molecular weight (see ESI, Figure S38 and S40).

The synthesized PU have also been subjected to thermal characterization. Differential Scanning Calorimetry (Perkin Elmer DSC6) was used to analyse the thermal transitions by applying the following thermal treatment: i) heating from $-70\text{ }^\circ\text{C}$ to melting at $20\text{ }^\circ\text{C}/\text{min}$ (first scan); ii) cooling from the final temperature to $-70\text{ }^\circ\text{C}$ at $100\text{ }^\circ\text{C}/\text{min}$; iii) heating from $-70\text{ }^\circ\text{C}$ to melting at $20\text{ }^\circ\text{C}/\text{min}$ (second scan). Melting temperature (T_m) and enthalpy (ΔH_m) were considered as the maximum and the underlying area of the melting peak, respectively.

Thermogravimetric analysis (Perkin Elmer TGA7), was employed to evaluate the thermal stability by heating from 50 to $800\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The 5% weight loss and maximum degradation rate temperatures ($T_{5\%}$ and T_{max}) were calculated.

Results and discussion

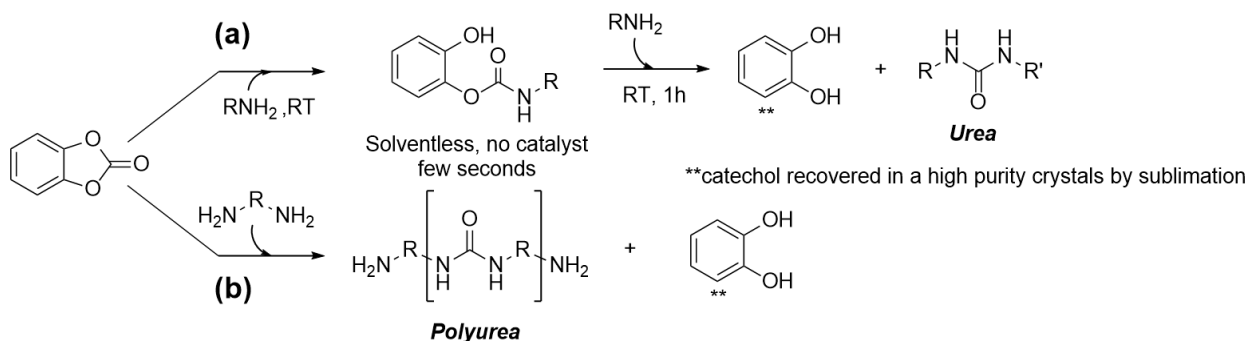
The reactivity of catechol carbonate (CC) has been firstly investigated and optimized for the synthesis of symmetric di-substituted urea, focusing the attention on the reaction conditions to maximize the yield, reducing the reaction time and investigating the best procedure to recover unreacted amine and co-produced catechol for successive recycle. On this basis, the polymerisation tests were conducted scaling up the amount of reactants.

The synthesis of *N,N'*-disubstituted urea

The reactivity of CC with *n*-butylamine (with an amine:CC molar ratio of 10) to yield 1,3-dibutylurea was firstly investigated at room temperature under stirring in a simple screw-cap vial. Interestingly, without the need of any catalyst and solvent, the reaction was complete within 1 hour at 25°C. NMR characterization of the reaction mixture recovered in DMSO- d_6 (Figure S1 and S2) showed the quantitative formation of 1,3-dibutylurea.

Moreover, we found that the reaction is general for several primary aliphatic amines and is independent from the steric hindrance of the substrate (Table 1). It takes place in very mild conditions (room temperature, atmospheric pressure), is characterized by low reaction time (1h), slight excess of amine (5 times the stoichiometric amount) behaving as solvent and, finally, it shows complete selectivity toward the desired products. Noteworthy, a quantitative formation of the corresponding diphenyl urea was achieved in 2h also using the lower nucleophilic aniline.

In principle, the reactions proceed through the nucleophilic attack of the amine's nitrogen on the hard electrophilic site of CC (the carbonyl carbon) with the formation of a carbamate intermediate, which is consecutively converted into the urea with only catechol as the co-product (Scheme 2).



Scheme 2. Catechol carbonate reaction with amines (route a) and diamines (route b) to yield urea and polyurea, respectively.

However, the carbamates were not detected in the NMR analyses of the final reaction mixtures (as reported in Table 1), probably being the consecutive nucleophilic substitution to yield the urea too fast (see ESI, Figures S1-S10).

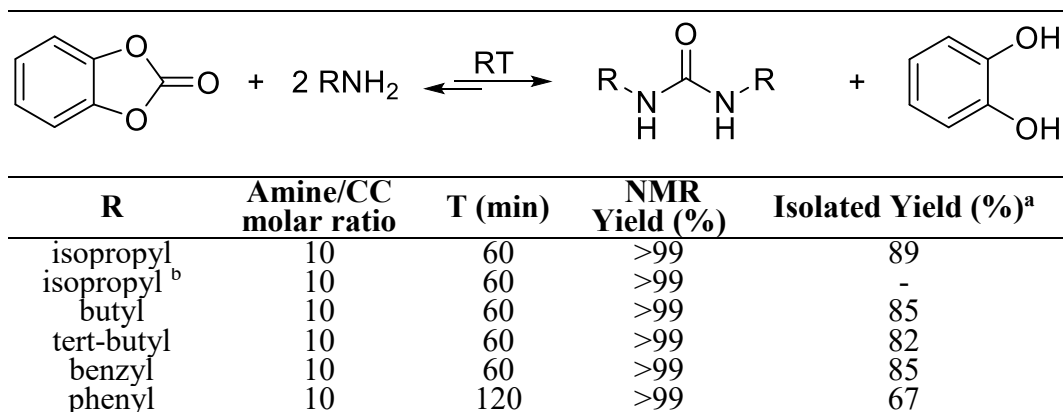


Table 1. The reaction of catechol carbonate (CC) and amines to yield N,N'-disubstituted urea and catechol. General conditions: solvent-less, room temperature. CC conversion was always complete. ^a Isolated yields obtained by the complete sublimation of catechol from the residual solid. ^b Test performed by scaling up the synthesis to 1mmol of CC (instead of 0.15 mmol).

Interestingly, in all the reactions investigated, the precipitation of a solid was observed, which correspond to the substituted urea. When isopropylamine, as an example, was the reagent (CC:amine molar ratio equal to 10, room temperature, 1h), the precipitation of a white solid was observed after 15 minutes only. After the reaction, the solid was filtered and washed with cold (ca. 0°C) isopropylamine, leading to di-isopropyl urea with an isolated yield of 61% (GC-MS). As a matter of fact, the solubility of the target product in the parent amine phase was low enough to allow the precipitation, finally helping the shifting of the equilibria toward the products side. However, part of the urea was lost during the washing step, limiting the isolated yield achievable (far from the quantitative yield observed by NMR). For these reasons, in the case of lighter aliphatic amines (*n*- and *t*-butyl, isopropyl) an alternative purification procedure was set up. Firstly,

the excess of amine was recovered by means of distillation under vacuum at room temperature. In this way, from 82 to 88% of the unreacted amines could be recovered and recycled for another synthesis. The obtained solid mixture containing both the product and catechol was heated in vacuum (60 °C, 1 mbar) in order to promote the sublimation of the aromatic diol in a few hours. The latter could be quantitatively recovered as pure crystals in a cold trap and recycled without any further purification for the preparation of fresh CC. By increasing the sublimation temperature up to 100-150 °C, the isolation of pure urea in high yield (Table 1) was also achieved.

In the case of dibenzyl and diphenyl urea, characterized by higher boiling point (184-185 °C), a further different purification procedure was employed. After the reaction, water was added as a non-solvent promoting the precipitation of the urea, which was then filtered and washed with water leading to the isolated yields reported in Table 1. The differences observed in the obtained isolated yields can be easily attributed to the different procedures applied in order to recover and quantify the target products. Indeed, while for the lighter amines the products were recovered after catechol sublimation, in the case of dibenzyl and diphenyl urea, in which parent amines are characterized by higher boiling points (184-185 °C), after the reaction, water was added as a non-solvent promoting the precipitation of the urea. In our opinion, the differences observed in the isolated yields for isopropyl, *n*-butyl and *t*-butyl urea are mainly due to differences in the volatility and thermal stability of these compounds. Similarly, the lower yield obtained for the diphenyl urea compared to the dibenzyl urea is only due to an increased tendency to undergo hydrolysis when water is added as non-solvent. With the final aim of eliminating one of the two purification steps, the reactions with isopropyl-, *n*-butyl- and benzyl-amines were carried out by feeding the stoichiometric amount of reagents (Table 2).

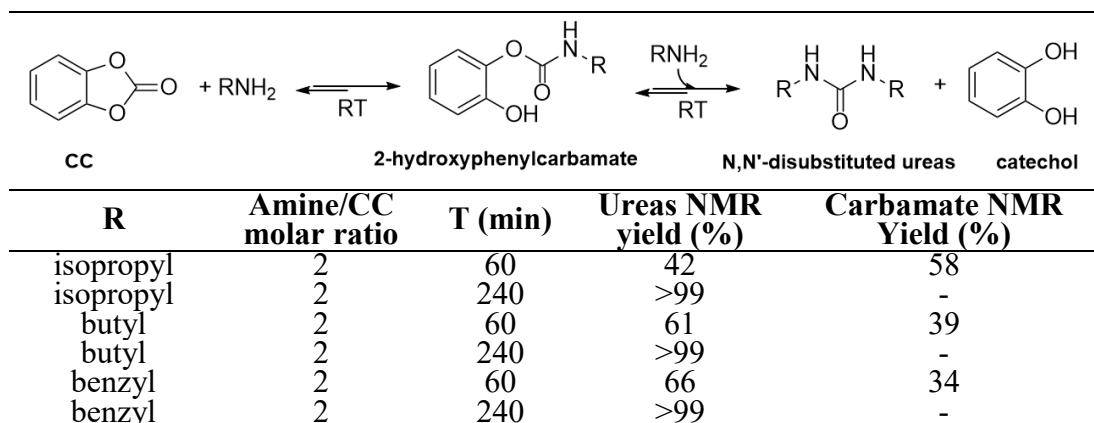


Table 2. The reaction of catechol carbonate (CC) and amines to yield N,N'-disubstituted urea and catechol. General conditions: solvent-less, room temperature. CC conversion was always complete.

Noteworthy, also in these cases, the reactions showed high selectivity and yield, however requiring longer reaction time. For a possible application at a larger scale, the increase of reaction time is less economically disadvantageous compared to the under-vacuum evaporation of amine because of the elimination of a step and the consequent reduction of energy consumption.

Interestingly, by analyzing the reaction mixture after 60 minutes, the formation of the intermediate carbamate was confirmed by NMR. Wondering about both the reaction pathway and the nature of the rate determining step, the reaction of a slight molar excess of isopropyl amine and CC (amine:CC=5:1), was followed by *in situ* ¹H-NMR experiments in DMSO-d₆ (Figure S23). Surprisingly, the complete conversion of CC was achieved in less than three minutes with the concomitant formation of a mixture of 2-hydroxyphenylcarbamate and 1,3-diisopropylurea (Figure 2, a). Considering the dilution in DMSO-d₆, which is expected to slow down the reaction, this result is a clear indication of the great reactivity of CC, which, analogously to isocyanate, readily undergoes the reaction with amine without the need of neither catalyst nor heating.

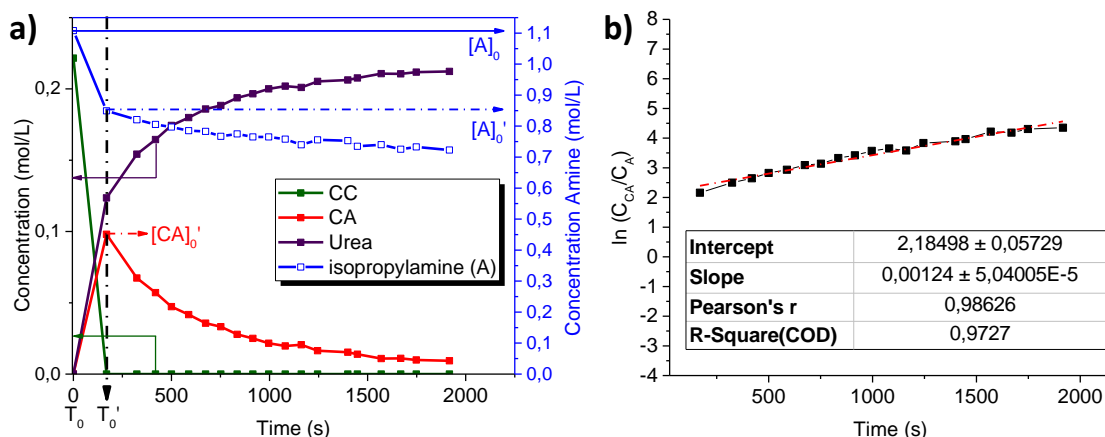
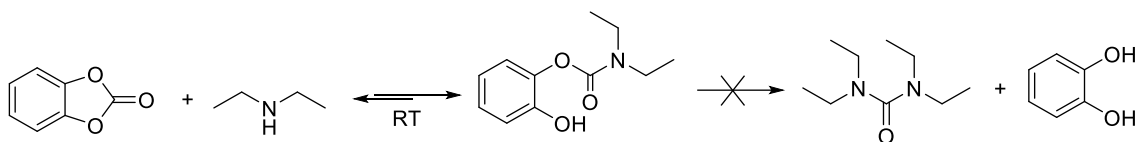


Figure 2. Concentration profiles of reagents and products of the reaction between CC and isopropyl amine (molar ratio: 1:5, RT), observed during the *in situ* $^1\text{H-NMR}$ test. CC: catechol carbonate, CA: 2-hydroxyphenyl-isopropyl carbamate, Urea: diisopropyl urea, A: isopropyl amine (Figure 2, a). Kinetic behavior of the formation of urea in the same conditions as described above (Figure 2, b).

Thus, the conversion of the intermediate carbamate into the corresponding di-substituted ureas represents the rate determining step of the overall procedure. Plotting the results of the *in situ* NMR experiment as a function of time, it was possible to follow the reaction profile (Figure 2, a). Because of the limitation of the NMR technique, it was not possible to monitor the fast CC consumption but only to verify its complete conversion into the intermediate. It follows that CC showed a peculiar reactivity with no comparison with other carbonates analogues. This behavior is probably due to the simultaneous contribution of the release of the steric strain of the five-membered cyclic carbonate functional group, as well as to the enhanced stability of the leaving group (catecholate anion).

With the aim to obtain information about the kinetics of the rate determining step (conversion of the intermediate to urea), the approximation to consider the beginning of the reaction at T_0 ' (Figure 2, a) was made. Plotting the natural logarithm of the intermediate/amine concentration (Figure 2, b) versus the reaction time, a straight line with a positive slope is achieved. By repeating the experiment doubling the amine amount (Figures S24 and S25), a plot with the same slope was obtained, thus establishing a pseudo second order kinetic behavior, with a kinetic constant of $0,0012\text{ s}^{-1}$. Furthermore, by lowering the hindrance of the amine (butyl instead of isopropyl) it was possible to verify that the reaction is faster and proceeds with a kinetic constant of about $0,0015\text{ s}^{-1}$ (Figures S29-S31), an effect that was not possible to observe when the reactions were performed in neat.

On the other hand, a completely different behavior was observed by reacting CC with a secondary amine: diethylamine. In this particular case, the reaction resulted anyway in the rapid, selective and quantitative formation of 2-hydroxyphenyl diethylcarbamate,⁸⁷⁻⁸⁹ by reacting an excess (10 times) of the amine with CC at room temperature (Figures S11 and S12). The conversion of CC is complete within 5 minutes. However, we found that the second nucleophilic attack was disfavored, and the formation of the corresponding urea was not observed neither by waiting for longer reaction time, nor by increasing the reaction temperature to 55°C , i.e. at reflux conditions (Scheme 3). The fact that the second nucleophilic attack was disfavored is an additional proof that the rate determining step is the attack of the second amine to the carbamate. Noteworthy, 2-hydroxyphenyl diethylcarbamate is an interesting building block in the synthesis of phenol-based medicinal and natural products⁹⁰ usually obtained by hydroxylation of aryl carbamate derivatives with multiple reaction steps and under harsher conditions. This peculiar behavior, however, will be further investigated in the future and is not deepened in this manuscript.



Scheme 3. The reaction of catechol carbonate (CC) and diethylamine to yield 2-hydroxyphenyl diethylcarbamate.

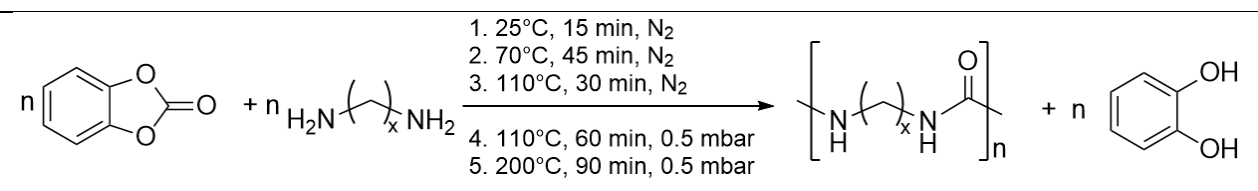
Finally, control tests have been performed using dimethyl carbonate (DMC) as carbonylating agent of selected amines in order to underline the advantages of our synthetic strategy. In particular, the reaction of DMC with isopropyl, n-butyl and diethyl amines have been performed in the same reaction conditions applied for the reaction of catechol carbonate (CC), namely: amine/DMC molar ratio of 10, 1 hour of reaction at room temperature and catalyst free conditions. Indeed, no reactions occurs and NMR analyses of the crudes shows the reaction mixture unvaried (see S41-S46), confirming the enhanced reactivity of CC (see supporting information for further details and comparisons with the most pertinent alternatives reported in literature).

The one-pot synthesis of polyurea

The above described synthetic strategy was then applied to the preparation of PU from CC and bio-based diamines, namely 1,4-butandiamine, 1,5-pentandiamine and 1,6-hexametilendiamine, which can be derived from amino acids (from lysine and ornithine, respectively) or from fermentation with genetically modified microorganism.

As stated in the experimental section, the polyurea polycondensation syntheses have been performed with higher amount of reactants for two main reasons: i) a proper mixing of the highly viscous system and ii) production of material quantities suitable for the functional property study. The synthesis of polyurea-x (x = 4, 5 and 6, Table 3), carried out without either solvent or catalyst, started at 25 °C, temperature at which CC is already active and low volatile oligomers can form.

Afterwards, the temperature has been progressively raised to favor the molecular weight increase, this latter proved by solidification, which takes place after 90 min from the beginning of the reaction process. At that point, the pressure has been reduced to promote recovering by sublimation of catechol, which accumulates in form of pure crystals and that can be effectively recycled in view of a green process (with an average recovery of 85%).



x	T (min)	Yield NMR (%)	M _n NMR (g/mol)	PU isolated yield (%)	Catechol Isolated Yield (%)
4	240	>99	1370	82	85
5	240	>99	1030	83	85
6	240	>99	3200	90	90

Table 3. The reaction of catechol carbonate (CC) and diamines to yield polyurea-x and catechol. General conditions: solvent-less, diamine:CC molar ratio = 1. CC conversion was always complete.

The outcome of the polymerization reaction was confirmed by NMR (Figure S38-S40) and infrared spectroscopy (Figure 3, top). As concern the FTIR analysis, besides the right-hand region (from 1550 to 500 cm⁻¹) usually referred to as fingerprint region and characteristic of each individual compound, the spectra collected clearly show for polyurea-4, polyurea-5 and polyurea-6, the typical stretching bands of carbonyl of the urea functional group and the amide stretching of CO-NH located at 1625 and 1550 cm⁻¹, respectively. At 3300 cm⁻¹, instead, the signal for the N-H stretch of amide group, proper of all the molecular structures predicted, is located. The peaks in between 3000 and 2800 cm⁻¹ are coming from the C-H bonds of the alkyl segments. It is worth

noticing the increasing of the C-H peak intensity with respect to the amide group signal, with the length of the aliphatic segment of the repeating unit.

The so conducted reaction leads to the M_n values reported in Table 3. The increase of the $-CH_2-$ group number in the repeating unit, from 4 for PU-4 to 5 for PU-5, has no effect on the molecular weight of the polymers as the corresponding M_n values are very similar (Table 3). This could be due to the modest M_n values, probably further increase of molecular weight being prevented by the solid state of the reaction mixture. In this regard, it could be interesting the use of diamines with an ad hoc structure leading to lower melting polymers that would be in the molten state under the described conditions and able to further react reaching higher molecular weight. On the other hand, the higher M_n value determined for polyurea-6 could be due to the greater length of the repeating unit that presents itself higher weight and, in turn, determines lower viscosity of the reaction system, with consequent possible proceeding of the polymerization process. Higher molecular weight polymer can be therefore achieved.

In the literature, examples of polyureas with comparable molecular weight are reported,⁸⁰ nevertheless, in some cases, the synthesis approach involves the use of large excess of the monomers (diamine and/or dimethyl carbonate).⁶¹ Polyureas and polyurea-based materials with higher molecular weight have been also obtained, nevertheless, the corresponding syntheses involve multi-step pathways and the use of solvents.^{63,78,79}

The PU obtained are insoluble in most organic solvents, because of their high crystallinity degree (evidenced by calorimetric analysis described in the following) and the inter-chain hydrogen bonds forming. In fact, NMR analysis has been carried out in TFA-d solvent (Figures S38-S40).

All the synthesized PU show high thermal stability (Table 4 and Figure 3 centre) making them suitable for high temperature applications. More in detail, approaching 300 °C, a gradual weight

loss of about 5% is observed, this last associated with the formation of volatile cyclic derivatives coming from the backbiting reaction of the ammine terminal groups.⁹⁰

Sample	DSC				TGA	
	I scan		II scan		T _{5%} (°C)	T _{max} (°C)
	T _m (°C)	ΔH _m (J/g)	T _m (°C)	ΔH _m (J/g)		
polyurea-4	375	730	-	-	283	355
polyurea-5	278	130	277	120	300	389
polyurea-6	292	120	290	100	305	380

Table 4. Thermal characterization data of polyurea.

The maximum degradation rate takes place at higher temperature: 355, 389 and 380 °C for polyurea-4, polyurea-5 and polyurea-6, respectively. The lower thermal stability of polyurea-4 can be ascribed to its intrinsic chemical structure characterized by higher density of ureic bonds along the macromolecular chain, these last responsible for the main degradation process involving isocyanate group formation.⁷⁸⁻⁸⁰ The PU calorimetric traces and data (Figure 3 bottom and Table 4) indicate the semicrystalline nature of the synthesized PU, characterized by very high melting temperatures, 375, 278 and 292 °C for polyurea-4, polyurea-5 and polyurea-6, respectively, as well as by huge melting enthalpies (ΔH_m). These values are in line with previous results.²⁰ The elevated T_m values evidence the presence of well-ordered crystal structure, coming from the high alkyl segment mobility and symmetry, and favored by the establishment of inter-chain hydrogen bonds. ΔH_m data indicate the high amount of crystal phase developed at the expense of the amorphous one, thus preventing the detection of the glass to rubbery transition step, being this latter associated to the amorphous portion. In the particular case of polyurea-4, the very huge area under the endothermic peak cannot be explained only as due to melting phenomenon. Indeed, the thermogravimetric analysis has shown the maximum degradation rate of polyurea-4 is at 355°C, i.e. before melting process starts. Consequently, the very high ΔH_m value suggests the phenomenon

of degradation is presumably taking place in concomitance with the melting process. As a matter of fact, no peaks are detected in the second scan, meaning the polyurea-4 macromolecules underwent degradation during the first heating step. Both polyurea-5 and polyurea-6 present lower melting temperatures and still high ΔH_m values indicating the amount of crystalline material is again predominant. The lower T_m and the higher thermal stability of polyurea-5 and polyurea-6 allow the materials melt without degrading, as confirmed by the second DSC scan acquired after melt quenching that, unlike polyurea-4, are practically the same as the first scans.

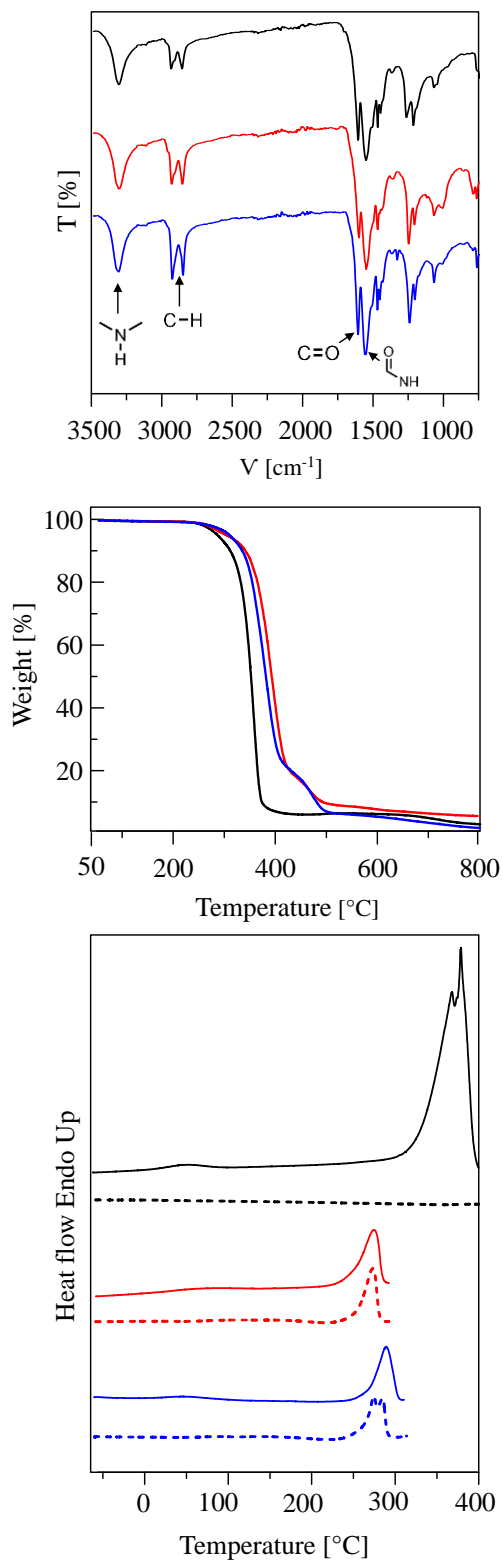


Figure 3. FTIR spectra (top), TGA curves (centre) and DSC traces (bottom) of polyurea-4 (black), polyurea-5 (red) and polyurea-6 (blue).

Conclusions

In summary, the peculiar reactivity of catechol carbonate as carbonylating agent for amines is herein reported. CC readily reacts with primary amines at room temperature and without the need of any additional catalyst or solvent, leading to the formation of the corresponding 2-hydroxyphenylcarbamate in few seconds (a reactivity more typical of the isocyanates). This carbamate intermediate undergoes the consecutive aminolysis reaction leading to the corresponding urea within one hour (or 2 hours for aniline). This versatile approach allows obtaining similar results despite the steric hindrance of both aliphatic and aromatic primary amine. CC peculiar reactivity is due to both the simultaneous contribution of the release of the steric strain of the five-membered cyclic carbonate functional group, as well as of the enhanced stability of the leaving group (catecholate anion).

The reaction is of general purpose unless for secondary amine, which leads anyway to the selective formation of substituted phenolic carbamates (e.g. 2-hydroxyphenyl diethylcarbamate), suitable as intermediates in medicinal chemistry.

Moreover, the novel synthetic pathway proposed for aliphatic and aromatic symmetric molecular urea, has been successfully extended to the one-pot preparation of polyurea. Indeed, to the best of our knowledge, CC and diamines have been never employed toward the selective synthesis of highly crystalline PU.

This novel synthetic strategy, which applies the high reactivity of CC to polymer synthesis, opens new perspective in the non-isocyanate route toward PU production, allowing the simple and effective recovery and recycle of both the excess of the amines (in the case of monomeric urea) and of catechol both in the molecular and, most importantly, in the polymer chemistry. CC is recovered as pure crystals by sublimation, obtaining excellent isolated recovery yields (from 85 to

100%). Furthermore, the possibility to employ bio-based building blocks, such as 1,4-butandiamine, 1,5-pentandiamine and 1,6-hexamethylenediamine as diamine monomers, makes this synthesis a step forward for the circular economy of polyurea. The incredible fast carbamate formation and subsequent aminolysis can be also connected to a new “click chemistry” concept for several applications (e.g. immobilisation of homogeneous catalysts over suitable supports, design of urea based organic catalysts or other suitable functionalization).

Acknowledgements

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Supporting Information. Supporting information are available containing: products and intermediate characterisation, NMR spectra, GC-MS.

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Superior reactivity of catechol carbonate toward aminolysis yielding urea and polyurea in mild, solvent and catalyst free conditions.

