Synthesis of Oxazolidinones, Dioxazolidinone and Polyoxazolidinone (A New Polyurethane) *Via* A Multi Component-Coupling of Aldehyde, Diamine Dihydrochloride, Terminal Alkyne and CO_2

Djamila Teffahi,[1, 2] Smain Hocine[1] and Chao-Jun Li*[2]

[1]*Laboratoire de Génie Chimique et Chimie Appliquée, Hasnaoua Université, Mouloud Mammeri, 15000 Tizi-Ouzou, Algérie*

[2]*Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal QC H3A 2K6, Canada*

Received January 23, 2012: Revised July 01, 2012: Accepted July 01, 2012

Abstract: In the present paper, the coupling reaction of aldehyde, terminal alkyne, amine salt and CO_2 was investigated. Copper iodide was found to be an efficient catalyst for the coupling reaction in ethyl acetate at 80 °C and under an atmospheric pressure of CO_2. A diverse range of oxazolidinones was prepared by this method. Subsequently, a copper-catalyzed coupling of aldehyde, terminal alkyne, diamine salt and CO_2 was developed to generate a dioxazolidinone. Finally, under the optimised conditions, we report for the first time a facile synthetic route for the synthesis of polyoxazolidinone, a new polyurethane, via a multi-component coupling of benzaldehyde, 1, 4-diethynylbenzene, 1, 6-hexadiamine and CO_2.

Keywords: Carbon dioxide fixation, copper catalysis, multicomponent reactions, oxazolidinone, polyurethane.

1. INTRODUCTION

While the increased atmospheric carbon dioxide level [1] has caused major concerns, [2] opportunity arises for the development of commercially viable routes to basic chemicals that employ carbon dioxide as the starting material [3]. Fixation of CO_2 by transition-metal catalysts has made significant progress recently. One of the successes is the utilization of propargylic alcohol derivatives and carbon dioxide as the starting materials to prepare cyclic carbonates in the presence of a metal catalyst such as ruthenium, [4] cobalt, [5] palladium [6], and copper [7] or phosphine compounds [8]. Another protocol in which CO_2 has been utilized as a substrate is through the carboxylative cyclization of propargylic amines to generate oxazolidinones bearing exocyclic alkenes. For example, propargylic amines have been reacted with CO_2 in the presence of organometallic complexes of ruthenium [9] and palladium [10]. Catalyst-free versions of the carboxylative cyclization of propargylamines with CO_2 have also been achieved using strong bases, [11] in supercritical CO_2 [12] and under electrochemical conditions [13]. However, these cyclisation protocols of propargylic alcohols and propargylic amines are often carried out under a high pressure of CO_2.

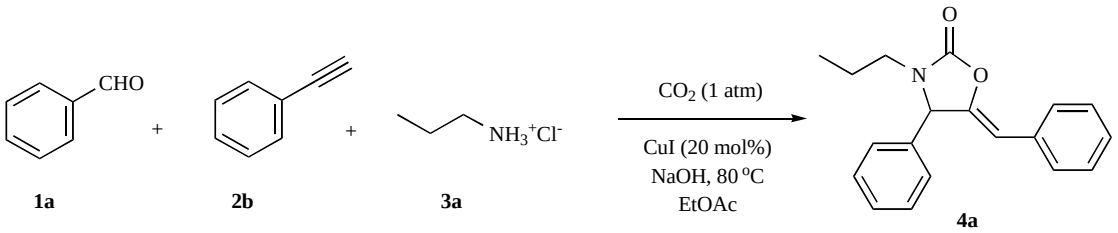
Polyurethanes (PUs) are among the most important and versatile classes of polymers and can vary from thermoplastic to thermosetting materials [14]. The industrial production of PUs is normally accomplished through the co-polymerization reaction between organic isocyanates and compounds containing active hydroxyl groups, such as polyols. Usually, both isocyanates and polyols for polyurethane productions are petroleum based.

Renewable resources are recently gaining considerable attention as petroleum substitute in producing polymers [15]. In this context, there have been a large number of publications on the use of vegetable oil as a starting material for polymers, which offers numerous advantages such as low toxicity, inherent biodegradability, and high purity [16]. The development of new routes to (functional) polymers comprising urethane groups without using isocyanates was also investigated. An isocyanate-free preparation of polyurethane was reported by reacting diamines with a cyclic carbonate (EC or PC), or from the reaction of diphenyl carbonate, and a glycol (ethylene glycol or 1, 2-propanediol) [17]. Because polyurethanes offer extraordinary versatility and are used in many applications, more considerable attention has been paid to the synthesis of such polymers based on the development of simpler routes with the use of easily accessible and cheap reagents.

After successfully developed a wide range of catalyzed three-component coupling reactions between aldehydes, amines, and alkynes (A^3-coupling) to generate propargylic amines, [18] our group reported a tandem five-component double A^3-coupling [19] and a tandem six-component double A^3-coupling followed by a [2+2+2] cycloaddition reaction catalyzed by copper [20]. More recently, we also reported an efficient copper-catalyzed four-component, tandem A^3- coupling/carboxylative cyclization between aldehydes, amines, terminal alkynes and CO_2 in which CO_2 serves as both a promoter and a reagent for the facile synthesis of synthetically important oxazolidinone products [21].

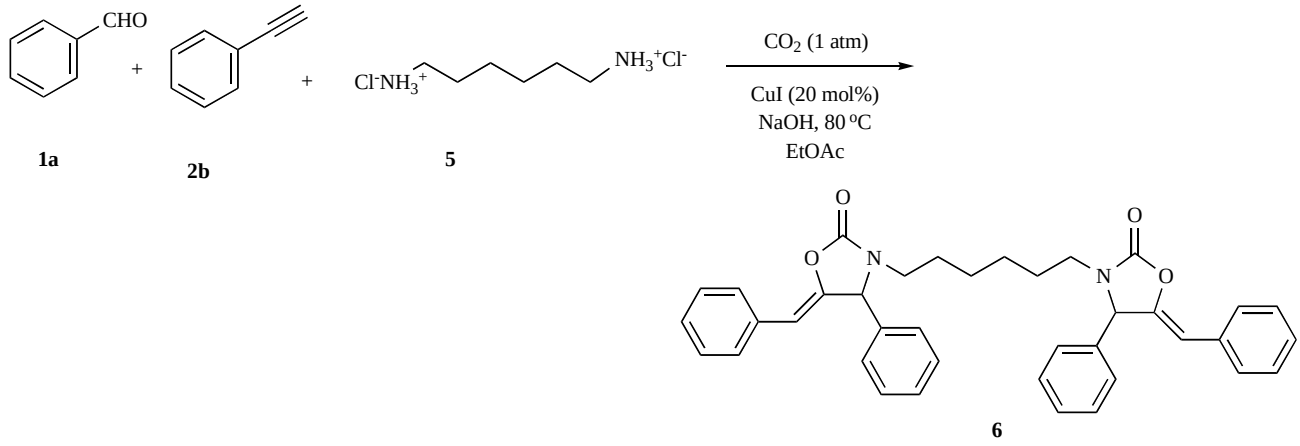
*Address correspondence to this author at the Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal QC H3A 2K6, Canada; Fax: (+1)-514-398-3797; E-mail: cj.li@mcgill.ca

1875-6255/12 $58.00+.00



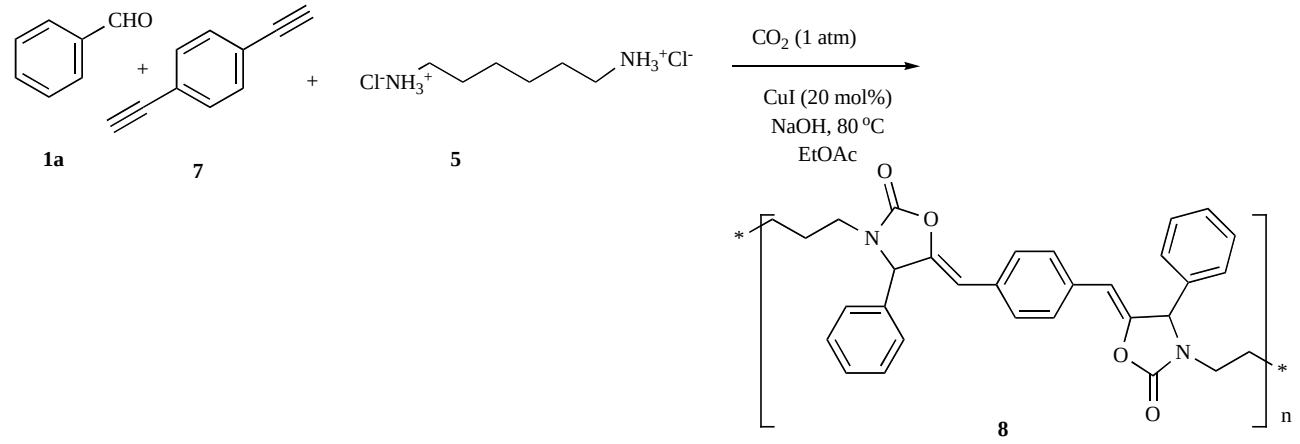
1a **2b** **3a** **4a**

Scheme 1. Oxazolidinone synthesis from aldehyde, alyne, amine salt and CO_2.



1a **2b** **5** **6**

Scheme 2. Dioxazolidinone synthesis from aldehyde, alkyne, amine salt and CO_2.



1a **7** **5** **8**

Scheme 3. Polyoxazolidinone (polyurethane) synthesis from aldehyde, alkyne, amine salt and CO_2.

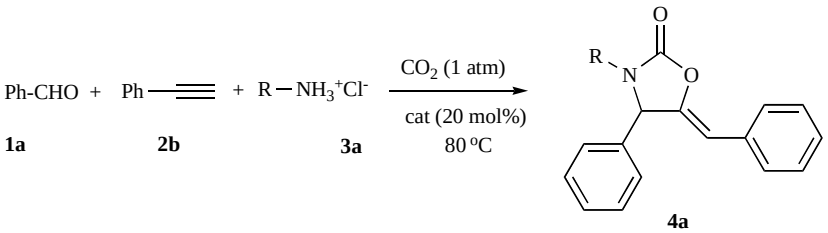
As part of our ongoing research on the utilization of A^3-coupling, we conceived a new route to polyurethane under mild conditions directly from CO_2, an alkyldiamine (ideally renewable amino acid salts), a diyne and an aldehyde. Because of the wide availability and high stability of amines in salt forms (such as amino acids), we focused our investigation with the study of the feasibility of simple oxazolidinone synthesis *via* a multi-component coupling of aldehyde, amine salt (amine hydrochloride), alkyne and CO_2 at atmospheric pressure in the present of a base. Herein we wish to report a copper-catalyzed synthesis of oxazolidinone, a dioxazolidinone, and a polyoxazolidinone (a form of polyurethane) *via* a multi-component coupling of an aldehyde, an amine salt, and an alkyne under an atmospheric pressure of CO_2 under basic conditions.

2. RESULTS AND DISCUSSION

2.1. Oxazolidinone Synthesis

In an optimization study, we began with the oxazolidinone synthesis by coupling benzaldehyde, phenylacetylene and propylamine hydrochloride using copper iodide as catalyst under an atmospheric pressure of CO_2 (Table **1**). The cyclization reaction was carried out using different solvents under various reaction conditions. We also examined various transition metal salts to catalyze this coupling reaction. Unfortunately, almost all metals including silver that was expected to catalyze both the A^3-coupling reaction to generate propargyle amines and CO_2 fixation on the propargylamines or propargyl alcohols to generate oxazolidinone or cyclic carbonates, [22] was inert in this reaction. CuI, the catalyst

Table 1. Optimization of the Four-component Coupling between Alkyne, Aldehyde, Amine Salt and CO_2.



1a **2b** **3a** **4a**

Entry	Catalyst	Solvent	Base	Yield (%)
1	CuI	Neat	NaOH ^{Aq}	<5
2	CuI	Neat	NaOH ^{s}	34
3	CuI	Neat	KOH ^{s}	20
4	CuI	Neat	$Ba(OH)_2$ ^{s}	<5
5	CuI	Neat	Li(OH)	<5
6	CuI	EtOH	NaOH^{S}	<5
7	CuI	H_2O	NaOH ^{s}	36
8	CuI	EtOAc	NaOH^{s}	71
9	CuI	Toluene	NaOH^{s}	34
10	CuI	THF	NaOH^{s}	12
11	CuI	DMSO	NaOH^{s}	trace
12	CuI	CH_3CN	NaOH^{s}	43
13	CuI	DMFA	NaOH^{s}	5
14	CuI	DMAc	NaOH^{s}	5
15	CuI	DCE	NaOH^{s}	37
16	CuI	DCM	NaOH^{s}	23
17	CuBr	EtOAc	NaOH^{s}	7
18	$CuBr_2$	EtOAc	NaOH^{s}	13
19	Cu(0)	EtOAc	NaOH^{s}	<5
20	AgCl	EtOAc	NaOH^{s}	trace
21	AgBr	EtOAc	NaOH^{s}	0

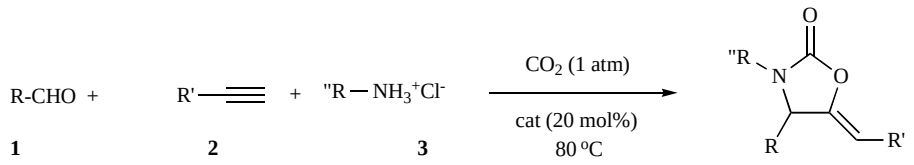
Conditions: all reactions were carried out on a 0.25 mmol scale with phenylacetylene (1.5 equiv), benzaldehyde (1.0 equiv), propyl amine hydrochloride (1.0 equiv), and copper catalyst (20 mol %) in solvent (0.2 mL) under CO_2 (1 atm). Reported yields based on **1a** and determined by ^{1}H-NMR using an internal standard.

that we used for the oxazolidinone synthesis with amine, [21] was found to be also suitable with amine salt in combination with a base with the modification of reaction conditions.

The screening of a range of solvents showed that the solvent had a strong effect on the reaction (Table **1**, entry 5): in the same solvent (ethanol) used previously for oxazolidinone synthesis with free amine, [21] only a trace amount of the desired product was obtained (Table **1**, entry 6). Table **1** shows that THF, DMSO, DMFA, DMAc were less suitable solvents for this coupling reaction (Entries 10, 12, 13 and 14), and the desired product was obtained in very low yields (yield < 5) at 80°C even after stirring for 24 h. The tandem reaction proceeded smoothly under neat conditions as well as in water, toluene, dichloroethane or dichloromethane to offer the oxazolidinone in moderate yields (Table **1**, entries 2, 7, 9, 12, 15 and 16). Using ethyl acetate as solvent, compound **4a** was obtained in 71% yield in the presence of 2 equiv of a strong base such as NaOH (solid form) (Table **1**, entry 8). Bases other than NaOH were tested. KOH could be used and lead to 20% yield in neat conditions (entry 2) but $Ba(OH)_2$, K_2CO_3, LiOH afforded **4a** in only 0~5 % yield. It is clear that not only the basicity but also the kind of cation affects the reaction (Table **1**, entries 2-5).

The optimized catalytic system was successfully applied to various combinations of alkynes, aldehydes and amine salts (Table **2**). In the presence of 20 mol % of CuI under an atmospheric pressure of CO_2 at 80 °C, the benzaldehyde, phenylacetylene together with propylamine hydrochloride, 2-phenylethylamine hydrochloride or 2-hydroxylethylamine hydrochloride were converted into the corresponding oxazolidinone in 71%, 70% and 71% yields, respectively (En-

Table 2. Copper-catalyzed four Coupling between Alkyne, Aldehyde, Amine Salt and CO_2.



1 **2** **3** **4**

Entry	R	R'		R''	Product	Yield (%)
1	Ph	Ph	Pr		**4a**	71
2	Ph	Ph	Ph-CH_2-CH_2-		**4b**	70
3	Ph	Ph	HO-CH_2-CH_2-		**4c**	71
4	Ph	Ph	Br-$(CH_2)_2$-CH_2-		**4d**	10
5	4-MeC_6H_4-	Ph	Pr		**4e**	44
6	4-BrC_6H_4-	Ph	Pr		**4f**	60
7	4-HOC_6H_4-	Ph	Pr		**4g**	64
8	4-MeOC_6H_4-	Ph	Pr		**4h**	40
9	4-CNC_6H_4-	Ph	Pr		**4i**	20
10	C_6H_{11}-	Ph	Pr		**4j**	20
11	Ph	3-HOC_6H_4-	Pr		**4k**	45
12	Ph	3-FC_6H_4-	Pr		**4l**	44
13	Ph	4-ButylC_6H_4-	Pr		**4m**	30

Conditions: All reactions were performed at 0.25 mmol scale with alkyne (1.0 equiv), aldehyde (1.0 equiv), amine salt (1.0 equiv) and CuI (20 mol%) in EtOH (0.2 mL) under CO_2 (1 atm). Isolated yields based on the aldehyde.

tries 1-3). However, the use of bromopropylamine hydrobromide resulted in a low yield of the corresponding product (Table **2**, entry 4).

Next, we examined the effect of varying the aldehyde component of the tandem reaction (Table **2**, entries 5-9). In general, it appears that the four-component reaction is very sensitive to the electronic properties of the aldehyde. Deviation from the benzaldehyde to either a more electron-rich or electron-poor aromatic aldehyde decreased the yield (Table **2**, entries 5-9). An aliphatic aldehyde such as cyclohexanal was also a viable substrate and provided the desired oxazolidinone in a moderate yield (Table **2**, entry 10). Finally, the alkyne component of the tandem reaction was examined (Table **2**, entries 9-11): the oxazolidinones were also obtained in moderate yields when aromatic alkynes bearing fluoro, hydroxyl and *tert*-butyl were used as substrates (Table **2**, entries 11-13).

2.2. Synthesis and Characterizations of Dioxazolidinone and Polyoxazolidinone

With the optimized conditions in hand and with the goal to prepare a polymeric oxazolidinone, as a model study, we first investigated the reactivity of 1, 6-hexadiamine salt in the coupling reaction with benzaldehyde, phenyl acetylene and CO_2 to prepare the corresponding dioxazolidinone **6** (Scheme **2**). Initially, we felt that 0.5 of diamine salt **5** is sufficient to generate the desired oxazolidinone in good yield. However, using 0.5 equiv of 1, 6-hexadiamine hydrochloride salt (**5**) with 0.5 or 1 equiv of NaOH, benzaldehyde **1a** (1 equiv) and phenylacetylene **2a** (1 equiv), under atmospheric pressure of CO_2 lead to the formation of dioxazolidinone **6** in a low yield of 20 and 27%, respectively. Also a moderate yield of 36% was obtained with the use of 1 equiv of diamine salt **5** with 1 equiv of NaOH; whereas a good yield (71%) of the dioxazolidinone product was obtained by using 1 equiv of diamine salt **5** and 2 equiv of NaOH. It is interesting to note that the mono-oxazolidinone was not detected, possibly due to the increased solubility of the intermediate (compared to the starting di-salt form) in the reaction solvent. We then contemplated the possibility to synthesize new polyoxazolidinone by using the tandem method.

Under the same reaction conditions, a good isolated yield (87%) of polyoxazolidinone **8** was obtained by the coupling of 1, 4-diethynylbenzene (**7**), benzaldehyde (**1a**), 1,6-hexadiamine dihydrochloride (**5**) and 2 equiv of sodium hydroxide under an atmospheric pressure of CO_2 at 80°C in ethyl acetate (Scheme **3**). The ^{1}H-NMR spectrum of the dioxazolidinone **6** is shown in Fig. (**1**). The proton bonded to the double bond appeared at 5.35 ppm and the characteristic protons of the oxazolidinone ring appeared at 5.25 ppm. The ^{13}C-NMR spectrum of the dioxazolidinone **6** and polyoxazolidinone **8** are shown in Figs. (**2** and **3**) respectively. In the dioxazolidinone spectrum, the carbonyl characteristic of the oxazolidinone ring appeared at 155 ppm (see ref 21). For the symmetric carbons of the hexyl bridge showed two peaks at 26.73, 25.93 and a peak at 41.63 corresponding to the carbon bonded to the nitrogen. In order to characterize the polyoxazolidinone **8**, various attempts were made to dissolve the

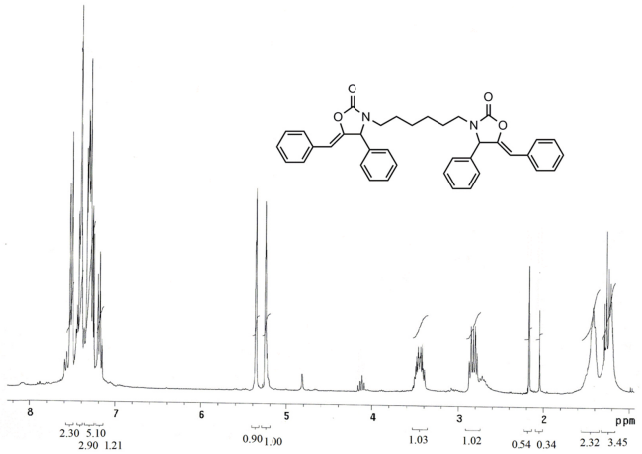


Fig. (1). [1]H-NMR of the dioxazolidinone (**6**).

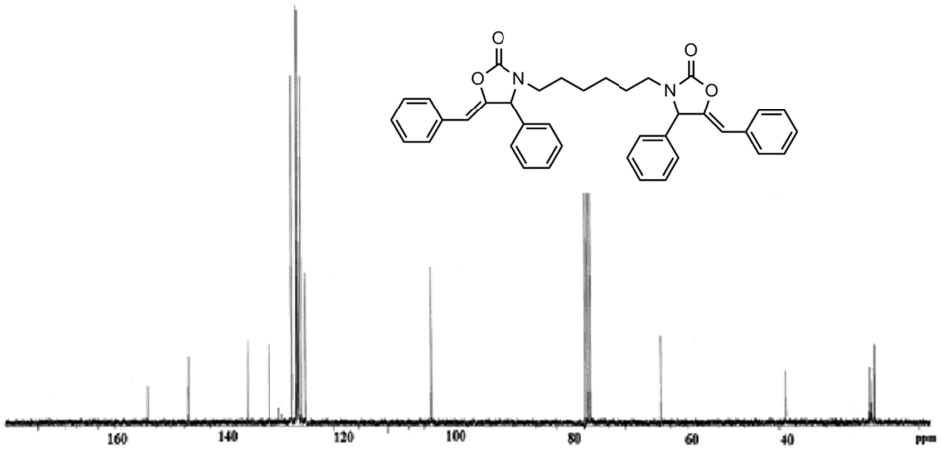


Fig. (2). [13]C-NM of the dioxazolidinone (**6**).

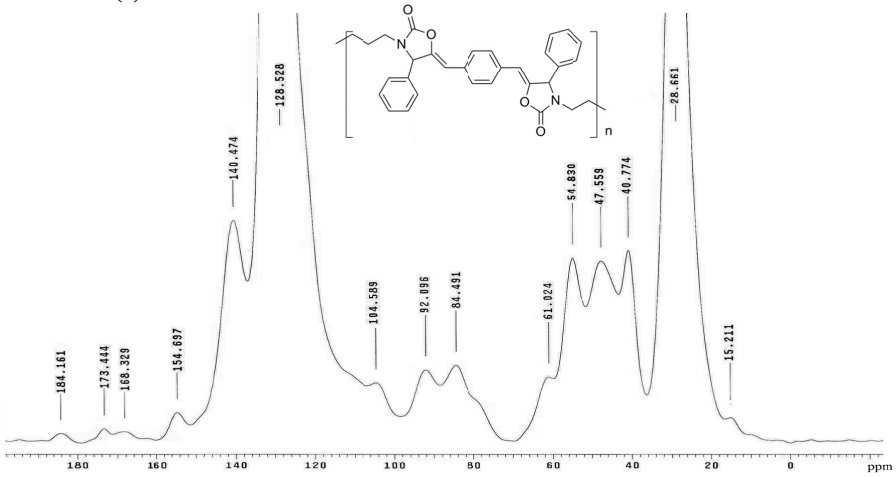


Fig. (3). [13]C-NMR of the polyoxazolidinone (**8**) at 25°C.

solid polymer with various solvents such as CH_2Cl_2, DMF, ether, THF, DMSO, $CHCl_3$, benzene, toluene and ethanol without any success. Subsequently, a solid state ^{13}C-NMR measurement was performed on the insoluble materials. Because of the symmetrical nature of the molecule we observed four peaks of the hexyl bridge at 1.15 ppm (4H), 1.40 ppm (4H), 2.80 polyoxazolidinone **8**. In the obtained ^{13}C-NMR spectrum there was overlap of the peaks of the carbons of the hexyl bridge and showed a large peak at around 41 ppm. The specific carbonyl signal of the oxazolidinone ring was also visible at 154.7 ppm. Additional peaks at 47.6, 54.8, 61.0, 84.9, 92.1, 168.3, 173.4, and 184.2 were visible and were attributed to the rest of unreacted benzaldehyde and its derivatives generated by Cannizzaro reaction.

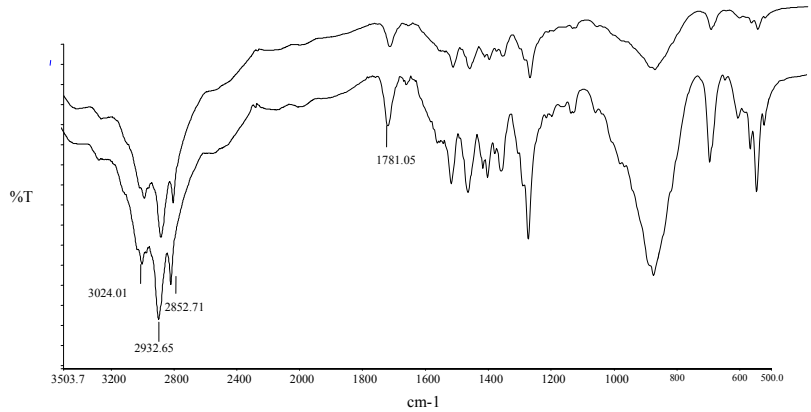


Fig. (4). FT-IR spectra of the polyoxazolidinone **8:** (-) fresh, (-) after heating at 130 °C.

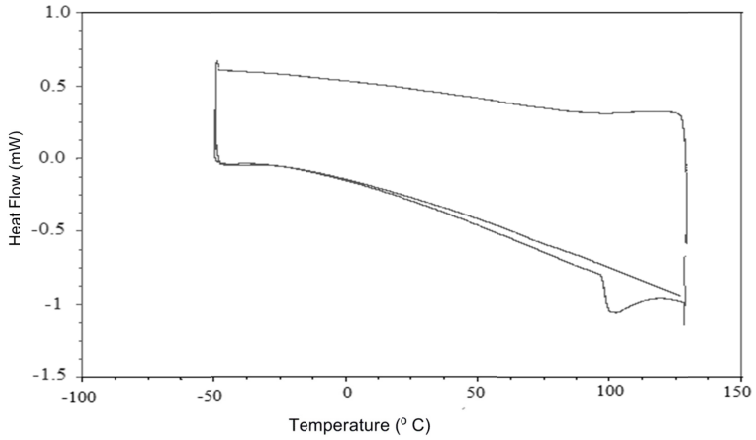


Fig. (5). DSC curve of the polyoxazolidinone **8** in N_2 at heating rate 20°C/min.

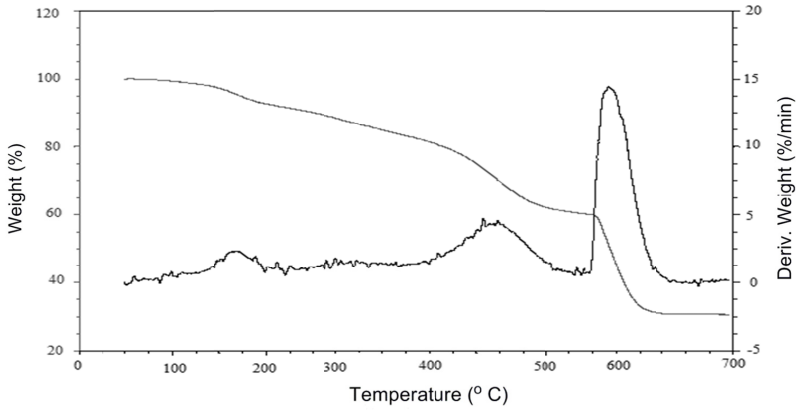


Fig. (6). TGA and DTG curves of the polyoxazolidinone **8** measured in N_2 at heating rate of 10°C/min.

The FT-IR spectrum of the polyoxazolidinone **8** is shown in Fig. (**4**). Another evidence of the formation of the polyoxazolidinone is the peak at 1781 cm^{-1} which was due to the the carbonyl group stretching of the oxazolidinone ring (see ref 16). The hexyl bridge showed peaks corresponding to the C-H bonds stretching at 2920 cm^{-1}. The phenyl groups showed peaks corresponding to the C-H bond stretching and bending at 3020 cm^{-1} and 697 cm^{-1} respectively. A visible small peak at 1730 cm^{-1} can be attributed to carbonyl of the unreacted benzaldehyde. It was noted that there was no characteristic peak of the free amine around 3300 cm^{-1}. The thermal properties of the polymeric oxazolidinone were investigated by Differential Scanning Calorimetry (DSC) (Fig. **5**) and Thermogravimetric Analysis (TGA) under nitrogen. In the DSC curve, a weak endothermic peak appeared at around 100°C with a small weight loss in the TGA curve. In an effort to determine just what may be the nature of this weight loss, a FT-IR analysis was carried out on dried polyoxazolidinone at 130°C. The resulting spectra (Fig. **4**) did not show any change in the characteristic peaks demonstrating that the lost weight was due to the rest of residue product such as water or solvent. The glass transition (Tg) was observed with a weak endothermic peak around 135°C in the DSC curve.

An exothermic peak was observed from 145°C with a weight loss in TGA curve. A FT- IR analysis was carried out for the polyoxazolidinone heated to the 232°C in order to check the nature of this lost weight. The peak characteristic to the carbonyl ring of the oxazolidinone (1781 cm^{-1}) disappeared in the FT-IR spectra demonstrating the decomposition of the polyoxazolidnone **8**.

3. CONCLUSION

In summary, we reported the use of carbon dioxide for the preparation of oxazolidinones, a dioxazolidinone and a polyoxazolidinone (polyurethane) *via* a copper-catalyzed multi-component coupling between aldehydes, amine salts, alkynes, and under atmospheric pressure of CO_2. Further studies on the scope of this novel method as well as efforts to increase the quality and to tune the properties of the polyurethanes are under further investigation.

4. EXPERIMENTAL

4.1. Materials and Measurements

All reagents were commercially available materials and were used without further purification.^{1}H NMR and ^{13}C-NMR spectra were recorded on Varian 400MHz, 300 MHz and 500MHz spectrometers. IR spectra were measured on a PerkinElmer FTIR. TGA and DSC were recorded on TGA Q500 and DSC Q2000 instrument.

4.2.1. Synthesis of the Mono-oxazolidinone (4a)

The oxazolidinone (**4a**) was prepared as following (Scheme **1**). A sealable test-tube equipped with a magnetic stir bar was charged with CuI (10.0 mg, 0.052 mmol), propylamine hydrochloride (**3a**) (24 mg, 0.25 mmol) and NaOH (10 mg, 0.25 mmol). The reaction vessel was sealed and flushed with CO_2. The tube was attached with a balloon of CO_2 and charged with EtOAc (0.2 mL), aldehyde **1a** (0.025 mL, 0.25 mmol), and then phenylacetylene (**2a**) (0.025 mL, 0.25 mmol). The reaction mixture was allowed to stir slowly at room temperature for approximately 30 sec (caution: reaction is slightly exothermic and will increase CO_2 pressure). The test tube was placed in an oil bath set at 80°C and was allowed to stir overnight. The reaction mixture was allowed to cool to room temperature and was passed through a plug of silica gel. The crude reaction mixture was further purified by silica gel column chromatography (hexane/EtOAc= 7:1) to provide the desired oxazolidinone **4a** as a yellow oil (51.21 mg, 71% yield). The ^{1}H-NMR and ^{13}C-NMR data are consistent with our previous report [21].

4.2.2. Synthesis of the Dioxazolidinone (6)

The dioxazolidinone was prepared similarly as described above by using 1, 6-hexadiamine dihydrochloride (**5**) (47 mg, 0.25 mmol) in place of propylamine hydrochloride and NaOH (20 mg, 0.5 mmol). The desired product **6** was obtained as a white solid in 71% yield, soluble in EtOAc, CH_2Cl_2 and $CHCl_3$. Rf=0.27 (EtOAc/Hexane: 1/9). FT-IR: 2924.51, 1761.06, 1690.26, 1598.07, 1492.60, 1448.99, 1418.71, 1346.64, 1275.87, 1259.56, 1203.99, 1182.88, 1157.51, 1094.00, 1071.31, 1037.92, 999.79, 946.25, 913.05, 863.67, 808.53, 775.78, 751.61, 726.11, 715.51, 690.45, 663.96, 625.74, 575.84cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$, ppm): δ= 7.93-7.7.59 (m, 4H), 7.45-7.40 (m, 6H), 7.37-7.29 (m, 8H), 7.25-7.16 (m, 2H), 5.38-5.33 (S, 2H), 5.28-5.23 (S, 2H), 3.48-3.42(m, 2H), 2.86-2.77 (m, 2H), 1.47-1.32(m, 4H), 1.31-1.17(m, 4H); ^{13}C-NMR (75MHz, $CDCl_3$, ppm): δ=155.1, 147.6, 137.2, 133.4, 129.4, 129.4, 128.4, 128.3, 128.0, 127.8, 127.0, 104.6, 63.9, 63.2, 41.6, 26.7, 25.9.

4.2.3. Synthesis of the Polymeric Oxazolidinone (8)

The polymeric oxazolidinone **8** was prepared by the same method as the preparation of the dimer **6**. With using benzaldehyde (**1a**) (0.025 mL, 0.25 mmol), 1, 6-hexanediamine dihydrochloride (**5**) (47 mg, 0.25 mmol), NaOH (20 mg, 0.5 mmol) and 1,4-diethynylbenzene (32 mg, 0.25 mmol) in ethyl acetate under an atmospheric pressure of CO_2 at 80°C (Scheme **3**). The product **8** was isolated as a colorless solid by filtration and then washed with water and dichloromethane. The product **8** was obtained in 87% yield. The polymer is insoluble in water and various organic solvents such as DMSO, benzene, THF, DMF, toluene, ethanol and CH_2Cl_2.

CHARACTERIZATION OF OTHER COMPOUNDS

- **(Z)-5-benzylidene-3-phenylethyl-4-phenyloxazolidin-2-one (4b)**: white solid; R_f=0.27 (EtOAc/hexane: 1/9); ^{1}HNMR (400MHz, $CDCl_3$): δ= 7. 45-7.55 (m, 2H), 7.38-7.45 (m, 3H), 7.22-7.38 (m, 6H), 7.18-7.24 (m, 3H), 7.8-7.16 (m, 2H). 5.17-5.16 (S, 1H); 5.06-5.05 (S, 1H); 3.79-3.72 (m, 1H); 3.11-2.19(m, 1H); 2.89-2.87 (m, 1H); 2.77-2.38 (m, 1H); ^{13}C-NMR (75MHz, $CDCl_3$): δ= 147.6, 138.1, 129.4, 129.3, 128.7, 128.7, 128.4, 128.31, 127.9, 126.9, 126.8, 104.5, 64.4, 43.2, 33.7. GC-MS: m/z= 355. The ^{1}H-NMR, ^{13}C-NMR data are consistent with our previous report [21].

- **(Z)-5-benzylidene-3-(2-hydroxyethyl)-4-phenyloxazolidin-2-one (4c):** Yellow liquid; Yield=71%; R_f= 0.27 (hexane/EtOAc: 7/1); ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.51-7.42 (m, 2H), 7.41-7.40 (m, 3H), 7.37-7.35 (m, 4H),7.33-7.29(m, 4H), 7.26-7.15 (m,1H), 5.58-5.56 (m, 1H), 3.81-3.66 (m, 2H), 3.62-3.53(m, 1H), 3.07-2.76 (m,1H); ^{13}C-NMR (75MHz, $CDCl_3$): δ= 155.8, 147.7, 137.2, 133.4, 129.4, 129.4, 128.5, 128.0, 128.0, 127.9, 127.0, 104.7, 65.0, 60.3, 44.4; GC-MS: m/z = 295.

- **(Z)-5-benzylidene)-3-propyl-4-(p-tolyl)oxazolidin-2-one (4e)**: pale yellow oil; Rf=0.27 (EtOAc/hexane: 1/9); ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7. 45-7.55 (m, 2H), 7.38-7.45 (m, 3H), 7.22-7.38 (m, 6H), 7.18-7.24 (m, 3H), 7.8-7.16 (m, 2H). 5.38-5.33 (S, 2H), 5.28-5.23 (S, 2H), 3.50-3.39 (m, 1H), 2.88-2.75 (m, 1H), 2.42-2.33 (s, 3H), 1.61-1.41 (m, 2H), 0.95-0.85 (m, 3H). ^{13}C-NMR (75MHz, $CDCl_3$): δ= 11.1; 20.3; 21.5, 43.5; 63.9; 104.5; 126.9; 127.8; 128.3; 128.4; 129.3; 129.4; 133.45; 137.3; 147.7; 155.1.

- **(Z)-5-benzylidene-4-(4-bromoyphenyl)-3-propyloxazolidin-2-one (4f):** yield=60%, yellow oil, R_f =0.48 (hexane/EtOAc: 3/2), ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.53-7.45 (m, 2H), 7.31-7.30 (m, 2H), 7.29-7.7.23 (m, 2H), 7.119-7.16 (m, 1H), 6.95-6.89 (m, 2H), 5.34-533 (S,1H), 5.24-5.23 (S, 1H), 3.43-3.37 (m,1H), 2.85-2.78

(m,1H), 1.53-1.46 (m, 2H), 0.89-0.85 (m, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): δ= 157.3, 147.9, 133.4, 131.6, 129.4, 128.5, 128.3, 128.0, 127.0, 116.3, 104.7, 63.6, 43.4, 20.3, 11.1.

• **(Z)-5-benzylidene-4-(4-methoxyphenyl)-3-propyloxazolidin-2-one (4h)**: yellow liquid, Yield=40%; R_f= 0.33 (hexane/EtOAc= 3/2); ^{1}H-NMR (400MHz; $CDCl_3$): δ= 7.55-7.54 (m, 3H); 7.51-7.18 (m, 4H); 6.96-6.88 (m, 2H), 5.35-5.34 (S, 1H), 5.25-5.24 (S, 1H), 3.85-3.80 (m, 3H), 3.45-3.34 (m, 1H), 2.86-2.75 (m, 1H), 1.55-1.43 (m, 2H), 0.95-0.83 (m, 3H); ^{13}C- NMR (75 MHz, $CDCl_3$): δ= 160.3, 155.0, 148.1, 133,5, 131.7, 129.2, 129.2, 128.8, 128.4, 128.3, 128.3, 126.9 114.6, 140.3, 63.4, 55.4, 43.1, 20.3, 11.1.

• **(Z)-4-(5-benzylidene-2-oxo-3-propyloxazolidin-4-yl)benzonitrile (4i)**: yellow oil, yield=20%, R_f=0.47 (hexane/EtOAc=7/1), ^{1}H-NMR (400MHz, $CDCl_3$): 7.53-50 (m, 2H), 7.45-7.40 (m, 2H), 7.34-7.25 (m, 4H), 7.21-7.15 (m, 1H), 5.39-5.38 (S, 1H), 5.25-5.24 (M, 1H), 3.48-3.40 (m, 1H), 2.86-2.77 (m, 1H), 1.55-1.45 (m, 2H), 0.89-0.85 (M, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): 147.70; 137.3; 133.4; 129.4; 129.3; 128.4; 128.3; 127.8; 126.9; 104.5; 63.8; 43.5; 20.3; 11.1.

• **(Z)-5-benzylidene-4-cyclohexyl-3-propyloxazolidin-2-one [4j]:** yellow oil, yield=20%, Rf=0.32 (hexane/EtOAc: 7/1); ^{1}H-NMR (400MHz, $CDCl_3$): 7.61-7.59 (m, 1H), 7.44-7.30 (m, 2H), 7.27-7.18 (m, 2H), 5.49-5.40 (S, 1H), 4.25-4.23 (S, 1H), 3.41-3.39 (m, 1H), 3.08-2.3.00 (m, 1H), 2.93-2.84 (m, 2H) , 2.65-57 (m,1H), 1.89-1.52 (m, 10H), 1.37-1.20 (m, 2H), 0.98-0.93 (m, 3H).

• **(Z)-5-(4-hydroxybenzylidene)-4-phenyl-3-propyloxazolidin-2-one (4k):** yellow oil, yield= 45%, R_f=0.32 (hexane/EtOAc: 7/1); ^{1}H-NMR (400MHz, $CDCl_3$): 7.58-7.55 (m, 1H), 7.42-7.38 (m, 1H) 7.37-7.21 (m, 3H) 7.20-7.15 (m, 3H) 6.99-7.85 (m, 2H) 5.35-5.33 (S, 1H) 5.11-5.09 (S, 1H) 3.48-3.40 (m, 1H), 2.86-2.77 (m, 1H), 1.55-1.45 (m, 2H), 0.89-0.85(M, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): δ= 156.2, 147.7, 137.1, 134.6, 129.7, 129.5, 129.4, 129.3, 128.7, 128.0, 127.8, 127.7, 104.6, 63.9, 43.6, 31.0, 20.3, 11.1.

• **(Z)-5-(3-fluorobenzylidene)-4-phenyl-3-propyloxazolidin-2-one (4l):** yellow oil, yield= 44%, ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.46-7.42 (m, 3H), 7.33-7.29 (m, 2H), 7.27-7.22 (m, 2H), 6.90-6.84 (m, 1H), 5.39-5.36 (S,1H), 5.23-5.21 (S, 1H), 350-3.40 (m, 1H), 2.86-2.77 (m, 1H), 1.54-1.45 (m, 2H), 0.89-0.84 (m, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): δ= 164.4, 161.2, 154.8, 148.8, 137.0, 129.8, 129.7, 129.4, 127.7, 124.1, 124.0, 115.1, 114.8, 113.9, 113.6, 103.5, 63.8, 20.3, 11.1.

• **(Z)-5-(4-(tert-butyl)benzylidene)-4-phenyl-3-propyloxazolidin-2-one (4m):** yellow oil, yield=30% , Rf=0.27 (hexane/EtOAc; 6/1); ^{1}H-NMR (400 MHz, $CDCl_3$): δ= 7.60-7.48 (m, 2H), 7.47-7.45 (m, 3H), 7.45-7.43 (m,3H), 7.26-7.25 (S, 1H), 5.38-5.37 (S,1H), 5.23-5.22 (S, 1H), 3.49-3.39 (m, 1H), 2.85-2.76 (m, 1H), 1.34-1.29 (m, 9H), 0.96-0.87 (m, 3H); ^{13}C-NMR (75MHz, $CDCl_3$): δ= 155.2, 150.0, 148.0, 130.6, 129.3, 129.3, 128.1, 127.8, 125.3, 104.4, 63.8, 43.5, 34.5, 31.2, 31.2, 20.3, 11.1.

CONFLICT OF INTEREST

The author(s) confirm that this article has no conflicts of interest.

ACKNOWLEDGEMENTS

DT thanks the Algerian MESRS for a fellowship for visiting McGill University. We are grateful to the Canada Research Chair (Tier I) foundation (to C.-J. Li.), the CFI, NSERC, and McGill University for support of our research. We also thank NMR Facilities Manager Department of Chemistry McGill University (to Dr. F. Morrin) for NMR analysis and Prof. R. B. Lennox for facilitating the FT-IR, TGA and DSC measurements.

REFERENCES

[1] Yamada, W.; Sugawara, Y.; Cheng, H.M.; Ikeno, T.; Yamada, T., Silver-catalyzed incorporation of carbon dioxide into propargylic alcohols. *Eur. J. Org. Chem.*, **2007**, 2604-2607.

[2] Sakakura, T.; Choi J.-C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev.*, **2007**, *107*, 2365-2387.

[3] a) Aresta, M.; Dibenedetto, A. The contribution of the utilization option to reducing the CO_2 atmospheric loading: research needed to overcome existing barriers for a full exploitation of the potential of the CO_2 use. *Catal. Today*, **2004**, *98*, 455-462; b) Aresta, M.; Dibenedetto, A. Utilisation of CO_2 as a chemical feedstock: opportunities and challenges. *Dalton Trans.*, **2007**, 2975-2992; c) Omae, I. Aspects of carbon dioxide utilization. *Catal. Today*, **2006**, *115*, 33-52.

[4] Sasaki, Y. Reaction of carbon dioxide with propargyl alcohol catalyzed by a combination of $Ru_3(CO)_{12}$ and Et_3N. *Tetrahedron Lett.*, **1986**, *27*, 1573-1574.

[5] Inoue, Y.; Ishikawa, J.; Taniguchi, M.; Hashimoto, H. Cobaltocene-catalyzed reaction of carbon dioxide with propargyl alcohols. *Bull. Chem. Soc. Jpn.*, **1987**, *60*, 1204-1206.

[6] a) Iritani, K.; Yanagihara, N.; Utimoto, K. Carboxylative coupling of propargylic alcohols with allyl chloride. *J. Org. Chem.*, **1986**, *51*, 5499-5501; b) Inoue, Y.; Itoh, Y.; Yen, I.-F.; Imaizumi, S. Palladium(0)-catalyzed carboxylative cyclized coupling of propargylic alcohol with aryl halides. *J. Mol. Catal.*, **1990**, *60*, L1-L3; c) Uemura, K.; Shiraishi, D.; Nozori, M. Inoue, Y. Preparation of cyclic carbonates from alkadienols, CO_2 and aryl or vinylic halides catalyzed by a palladium complex. *Bull. Chem. Soc. Jpn.*, **1999**, *72*, 1063-1070.

[7] a) Laas, H.; Nissen, A.; Nurrenbach, A. A simple synthesis of 3 H-indoles starting from acetylenic alcohols. *Synthesis*, **1981**, 958-959; b) Dimroth, P.; Pasedach, H. *Ger*., **1961**, 1098953; c) Dimroth, P.; Schefczik, E.; Pasedach, H. *Ger*., **1963**, 1145632.

[8] Joumier, J.M.; Fournier, J.; Bruneau, C.; Dixneuf, P.H. Functional carbonates: cyclic α-methylene and β-oxopropyl carbonates from prop-2-ynyl alcohol derivatives and CO_2. *J. Chem. Soc., Perkin Trans.*, **1991**, *1*, 3271-3274.

[9] Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. Ruthenium catalyzed selective synthesis of enol carbamates by fixation of carbon dioxide. *Tetrahedron Lett.*, **1987**, *28*, 4417-4418.

[10] b) Shi, M.; Shen, Y.-M. Transition-metal-catalyzed reactions of propargylamine with carbon dioxide and carbon disulfide. *J. Org. Chem.*, **2002**, *67*,16-21.

[11] a) Costa, M.; Chiusoli, G.P.; Rizzardi, M. Base-catalysed direct introduction of carbon dioxide into acetylenic amines. *Chem. Commun*., **1996**, 1699-1700; b) Costa, M.; Chiusoli, G.P.; Taffurelli, D.; Dalmonego, G.J. Superbase catalysis of oxazolidin-2-one ring formation from carbon dioxide and prop-2-yn-1-amines under homogeneous or heterogenous conditions. *J. Chem. Soc. Perkin Trans. 1*, **1998**, 1541-1546.

[12] Kayaki, Y.; Yamamoto, M.; Suzuki, T.; Ikariya, T. Carboxylative cyclization of propargylamines with supercritical carbon dioxide, *Green Chem.*, **2006**, *8*, 1019-1021.

[13] Feroci, M.; Orsini, M.; Sotgiu, G.; Rossi, L.; Inesi, A. Electrochemically promoted C-N bond formation from acetylenic amines

and CO_2. Synthesis of 5-methylene-1,3-oxazolidin-2-ones. *J. Org. Chem*., **2005**, *70*, 7795-7798.

[14] Lligadas, G.; Ronda, J.C.; Galià, M.; Cádiz, V. Oleic and undecylenic acids as renewable feedstocks in the synthesis of polyols and polyurethanes. *Polymers*, **2010**, *2*, 440-453.

[15] Gandini, A. Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules* **2008**, *41*, 9491-9504.

[16] a) Baumann, H.; Bühler, M.; Fochem, H.; Hisrsinger, F.; Zoeblein, H.; Falbe, J. Renewable raw materials for the chemical industry. *Angew. Chem. Int. Ed. Engl.*, **1988**, *27*, 41-62. b) Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J.O.; Klaas, M.R.; Schäfer, H.J.; Shneiderüsch, M.P. New syntheses with oils and fats as renewable raw materials for the chemical industry. *Angew. Chem. Int. Ed.*, **2000**, *39*, 2206-2224.

[17] a) Güner, F.S.; Yagci, Y.; Erciyes, T. Polymers from triglyceride oils. *Prog. Polym. Sci.*, **2006**, *31*, 633-670; b) Sharma, V.; Kundu, P. P. Polymers from natural oils—A review, *Prog. Polym. Sci.*, **2006**, *31*, 983-1008; c) Meier, M.A.R.; Metzger, J.O.; Schubert, U.S. Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev*. **2007**, *36*, 1778-1802; d) Y. Lu and R. C. Larock, Novel polymeric materials from vegetable oils and vinyl monomers: preparation, properties, and applications. *Chem. Sus. Chem.*, **2009**, *2*, 136-147.

[18] a) Li, C.-J. The development of catalytic nucleophilic additions of terminal alkynes in water. *Acc. Chem. Res.*, **2010**, *43*, 581-590; b) Chen, L.; Li, C.-J. Reaction of alkynes in water. *Adv. Synth. Catal*., **2006**, *348*, 1459-1484; c) Wei, C.; Li, Z.; Li, C.-J. The development of A^3-coupling (aldehyde-alkyne-amine) and AA^3-coupling (asymmetric aldehyde-alkyne-amine. *Synlett* **2004**, 1472-1483; d) W.-J. Yoo, L. Zhao, C.-J. Li, The A^3-coupling (aldehyde-alkyne-amine) reaction: A versatile method for the preparation of propargylamines. *Aldrichemi. Acta*, **2011**, *44*, 43-51.

[19] Bonfield, E. R.; Li, C.-J. Efficient ruthenium and copper cocatalzyed five-component coupling to form dipropargyl amines under mild conditions in water. *Org. Biomol. Chem.*, **2007**, *5*, 435-437.

[20] Bonfield, E. R.; Li, C.-J. Efficient preparation of the isoindoline framework *via* a six component, tandem double A^3 coupling and [2+2+2] cycloaddition reaction, *Adv. Synth. Catal.* **2008**, *350*, 370-374.

[21] a) Yoo, W.-J.; Li, C.-J. Copper-catalyzed four-component coupling between aldehydes, amines, alkynes, and carbon dioxide, *Adv. Synth. Catal.* **2008**, *350*, 1503-1506.

[22] **[21]** a) Huang, B.; Yao, X.; Li, C.-J. Diastereoselective aldehyde-alkyne-amine coupling of α-hydroxylated compounds, *Adv. Synth. Catal.* **2006**, *348*, 1528-1532; b) Wang, S.; He, X.; Song, L.; Wang, Z., Silver nanoparticles supported by novel nickel metal-organic frameworks: an efficient heterogeneous catalyst for an A^3 coupling reaction, *Synlett* **2009**, 447-450; c) Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. Silver-catalyzed enantioselective carbon dioxide incorporation into bispropargylic alcohols. *J. Am. Chem. Soc.*, **2010**, *132*, 4072-4073.

[23] Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. Silver-catalyzed preparation of oxazolidinones from carbon dioxide and propargylic amines. *Chem. Lett.* **2009**, *38*, 786-787.