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**Synthesis of Polyoxazolines Using Glycerol Carbonate Derivative and End Chains
Functionalization Via Carbonate and Isocyanate Routes**

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Keywords

Bio-based initiator, glycerol carbonate, polyoxazoline, telechelic polymer.

Abstract

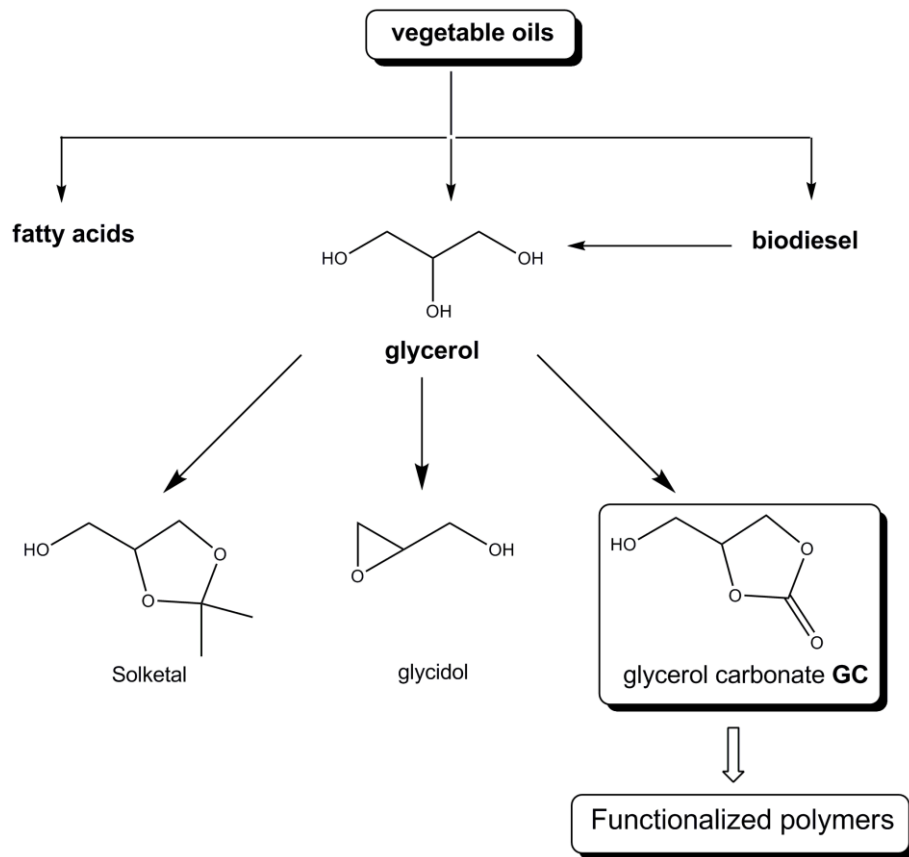
We report the cationic ring-opening polymerization of 2-methyl-2-oxazoline (**MOx**) using bio-based initiator (**GCTs**). The functional initiator **GCTs** was prepared by tosylation of the corresponding alcohol: glycerol carbonate (**GC**). The termination stage of the polymerization was achieved in presence of KOH and the telechelic polyoxazoline carrying five-membered cyclic carbonate and oxazolium end groups (**GC-POx^{ium}**) was converted to **((HO)₂-POx-OH)** carrying α -diol and ω -hydroxyl groups. End-functionalized polyoxazolines **(HO)₂-POx-OH** with M_n ranging from 4200 to 8400 g.mol⁻¹ were synthesized. According to GPC results, the polymerizations of **MOx** using **GCTs** and other initiator coming from 1,2-isopropylidene-glycerol (**Solk-Ts**) were compared. On the basis of FT-IR and NMR spectroscopies, the chemical modification of end chains of polyoxazolines was investigated by two alternative synthetic routes. The isocyanate route is a postpolymerization urethanization. The nucleophilic reactivity of the α -diol and ω -hydroxyl groups of **(HO)₂-POx-OH** was studied with functional isocyanate (**TESPI**). In the carbonate route, the electrophilic reactivity of α - and ω -end groups of **GC-POx^{ium}** were explored with amine. It was demonstrated that during the termination stage of the polymerization in presence of allylamine both urethane linker in α -end chain was synthesized and the ω -oxazolium group was converted into terminal amine. The carbonate route is an alternative to synthesize urethane without isocyanate.

Introduction

Poly(oxazoline)s have emerged recently as materials of importance in surface chemistry and in biomaterials science.[1] Polyoxazoline bearing short alkyl substituent, e.g., methyl or ethyl group, in the side 2-position are water-soluble. Among numerous water-soluble polymers, **POx**s are attractive for their low acute toxicity and have been approved by US Food and Drug Administration (FDA).[2,3] Functional polyoxazolines can be prepared either by the polymerization of functionalized oxazoline monomer or by the modification of telechelic **POx**. To prepare telechelic **POx**, functionalized group can be introduced at the initiation stage of the polymerization of 2-oxazolines (“initiator method”) or at the termination stage by reacting the living end of the propagating polymer with a nucleophile (“terminator method”). The synthesis of telechelic **POx** using molecules coming from renewable sources such as vegetable oils are currently underway in our laboratory.[4] Recently, industrial applications have emerged around the use of feedstock from renewable resources because sustainability will become increasingly important for the chemical industry.[5,6] Among them, fats and oils could become one of the major players in the chemical industry in the near future. Their competitive cost, worldwide availability, and built-in functionality make them attractive for numerous commercial applications. The growing production of biodiesel by transesterification of oil with methanol or ethanol is responsible for the overproduction of glycerine. Consequently, the price of glycerine has dropped dramatically. Glycerol is an intermediate in the synthesis of a large number of compounds used in industry (Solketal®: 1,2-isopropylidene-glycerol, glycerol carbonate, glycidol, dihydroxyacetone...) (Scheme 1).[7] A bio-based key bifunctional compound is glycerol 1,2-carbonate (**GC**, 4-hydroxymethyl-1,3-dioxolan-2-one) employed as a solvent,[8] additive, monomer,[9-10] and chemical intermediate. **GC** can be produced by transesterification of ethylene carbonate or

dimethyl carbonate.[11] In our strategy, glycerol carbonate **GC** was converted by tosylation in glycerol carbonate tosylate (**GCTs**) which was employed as functional initiator in 2-methyl-2-oxazoline (**MOx**) polymerization. The tosylation of **GC** has already been mentioned but the use of **GCTs** as initiator in polymer area has never been described to our knowledge.[12]

Herein, we report an easy route to synthesize functional polyoxazolines (**(HO)₂-POx-OH**) using **GCTs**. Kinetic study of the polymerization was investigated and the initiation step was examined in detail. Moreover the control of molecular weights was targeted and the molecular weights were compared to those obtained with other initiator coming from Solketal® (**Solk-Ts**). Before (**GC-POx^{ium}**) and after (**(HO)₂-POx-OH**) the termination stage of the polymerization, **POxs** carried carbonate, oxazolium end groups and diol, hydroxyl end groups, respectively. We explored the reactivity of the end groups in urethanization reactions. Usually urethane groups are prepared from isocyanate and alcohol reaction. An alternative route was also studied with the reaction of five-membered cyclic carbonate with amine which could afford Non Isocyanate PolyUrethane (NIPU).[13-15] The strategies were examined with model reactants. The further functional polymers can result in various materials with different properties to meet different application needs.

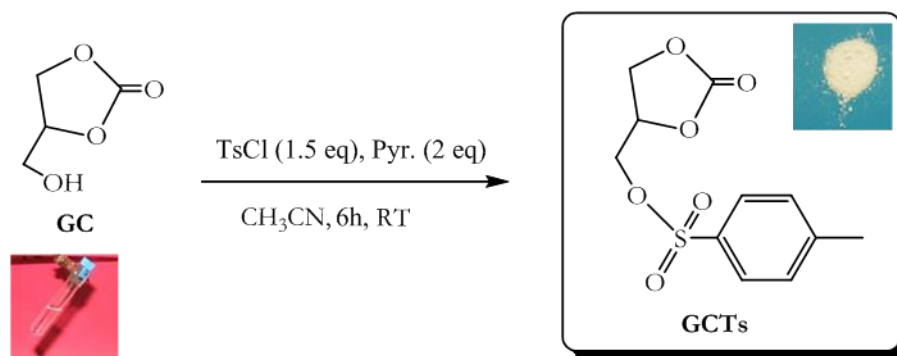


Insert Scheme 1.

Results and discussion

Synthesis of GCTs initiator

In order to synthesize functional polyoxazolines, we combined the use of bio-based functional initiator derivated from glycerol and the chain end modification. Carbonates based on glycerol, such as glycerol carbonate **GC**, are gaining interest due their simple preparation, versatile properties and chemical reactivity. Functionalization of hydroxyl function of **GC** was already investigated with various groups.[16] Starting from **GC** numerous compounds as glycerol carbonate tosylate **GCTs** have already been described in the literature by Tatibouët et al.[17] After 6h of reaction at RT, **GCTs** was easily isolated using the difference of physical characteristics of **GC** and **GCTs** as illustrated in Scheme 2. **GCTs** appears as a very interesting reagent due to the double electrophilic reactivity of tosylate and carbonate groups.

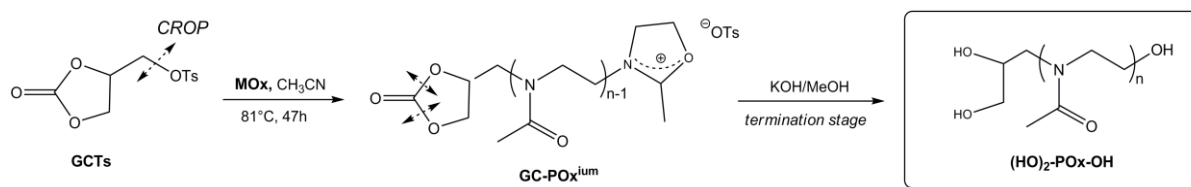


Insert Scheme 2.

Synthesis of (HO)₂-PO_x-OH polymer

In our work the polymerization of **MO_x** was investigated using **GCTs** as initiator of cationic ring-opening polymerization (CROP) as shown in Scheme 3. The CROP of **MO_x** was carried out in acetonitrile at 61 or 81°C. During the termination stage the propagating species **GC-**

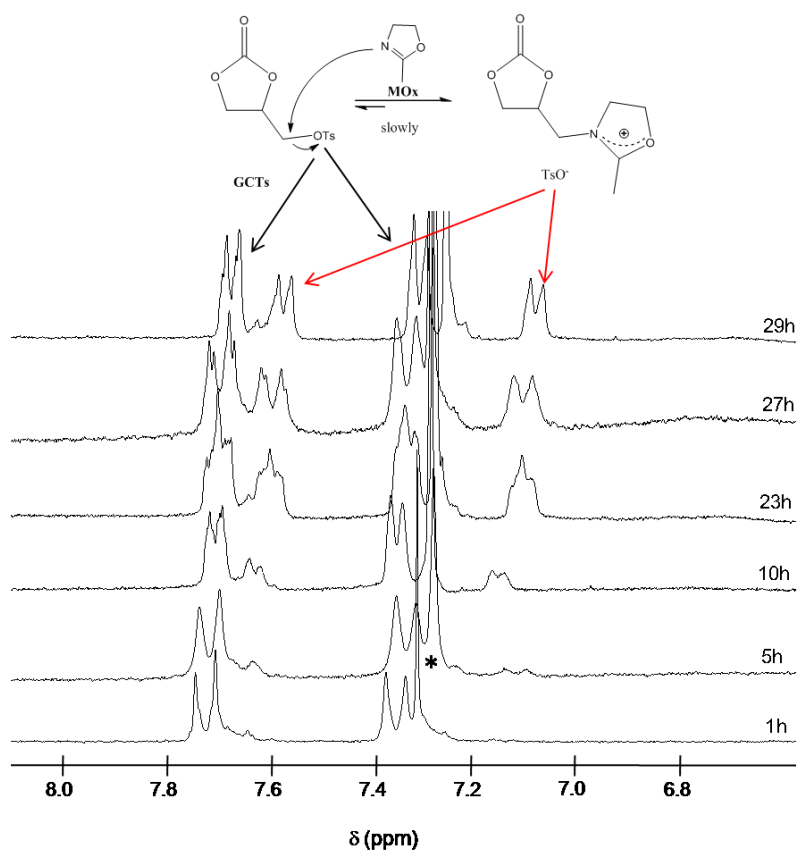
POx^{ium} reacted with a KOH-saturated methanolic solution at RT for 24h and gave $(\text{HO})_2\text{-POx-OH}$. The resulting $(\text{HO})_2\text{-POx-OH}$ was purified by slow precipitation from cold diethyl ether. In presence of KOH the carbonate and oxazolium end groups of $\text{GC-POx}^{\text{ium}}$ were converted into α -diol and ω -hydroxyl groups, respectively. The reactivity of five-membered cyclic carbonate group has been the subject of considerable research.[18,19] The carbonate protective group is base-labile and converted in situ to diol group without further step of deprotection. The complete conversion of carbonate group to diol group was checked by FTIR spectroscopy with the disappearance of the peak at 1765 cm^{-1} corresponding to C=O carbonate and the appearance of the peak assignable to O-H stretching at 3437 cm^{-1} . In a previous study, Binder et al. described the cationic ring-opening polymerization of MOx using a derivative of GC carrying a dioxolane group: **Solk-Ts** (Solketal®).[20] The conversion of dioxolane into diol end group was realized in a supplementary step under acidic conditions. In our case, the reactivity of carbonate group led in situ polymerization and end group deprotection (Scheme 3).



Insert Scheme 3.

The efficiency of GCTs as initiator in the MOx polymerization was investigated by ^1H NMR spectroscopy as illustrated in Figure 1. $[\text{GCTs}]/[\text{GCTs}]_0$ Ratio was calculated from the integration of the signals corresponding to aromatic protons of unreacted GCTs at 7.75 and 7.35 ppm in respect to signals corresponding to TsO^- specie in the polymer end chain at 7.65 and 7.10 ppm acting as counteranion of oxazolium propagating specie. TsO^- specie appeared

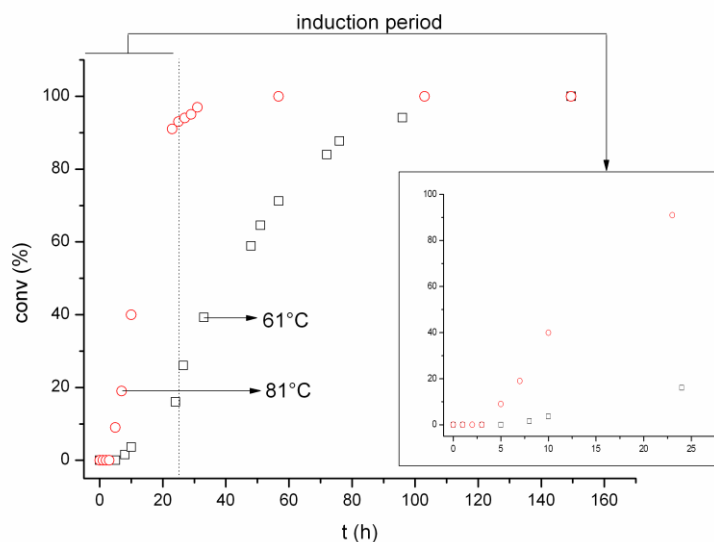
when the nitrogen of a **MOx** unit reacted onto **GCTs** initiator. The formation of TsO^- was slow and revealed a slow initiation step of the CROP of **MOx** using **GCTs**. In addition some unreacted initiator remained until complete monomer consumption and the calculated efficiency ratio of **GCTs** was around 60%.



Insert Figure 1.

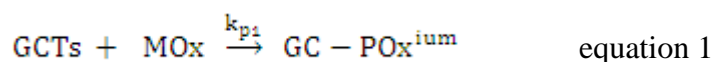
A preliminary kinetic study of cationic ring-opening polymerization of **MOx** using **GCTs** initiator was investigated. First **MOx** conversion versus time was determined for $\overline{DP}_n^{th} = 30$ by ^1H NMR experiments in CD_3CN as shown in Figure 2. The CH_2 protons of the monomer were observed at δ 4.4 and 3.7 ppm and shifted in a broadened peak at 3.5-3.1 ppm in the corresponding polymer. Their respective intensities were used to calculate the monomer concentration as a function of reaction time. The influence of the temperature on kinetic

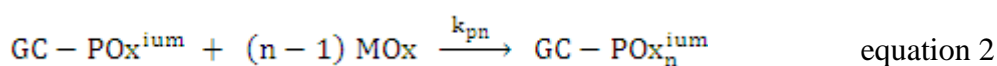
polymerization was studied at 61 and 81°C. Whatever the temperature the conversion was higher than 96% and the final reaction time logically decreased with the temperature. The final time was more than 3-fold at 81°C than 61°C.



Insert Figure 2.

Whatever the temperature a latency period was observed and ranged from 4 to 8 hours at 81 and 61°C respectively. The latency period during the CROP of **MOx** was also observed using others initiators.[21] The phenomenon may be related to quite different rate constants between the first step (k_{p1}) (Equation 1) and subsequent propagation steps (k_{pn}) (Equation 2) in the polymerization mechanism. The slow first propagation step could be explained by the stabilization of **GCTs** by interaction between carbonate and sulfonate groups of **GCTs**.[22] It has to be mentioned that the degradation of the cyclic carbonate did not occur at the early stage of the polymerization (checked by FTIR spectroscopy) and so could not explain the inhibition period.





Based on 1H NMR analyses, $\ln([M]_0/[M])$ versus reaction time revealed a downward curvature at the early stage of the polymerization corresponding to a decrease of growing centers concentration (Figure 3).[23] This non linear behavior at the early stage corresponds to the effect of slow initiation step on kinetics. After this period, $\ln([M]_0/[M])$ versus time was found to be linear indicating that the concentration of active chains remains constant throughout the polymerization i.e. no irreversible termination reaction occurred during polymerization. The linear part of $\ln([M]_0/[M])$ versus reaction time led to the determination of the rate constant of polymerization (k_{app}). The k_{app} s for the polymerization of **MOx** were calculated at 61 and 81°C. Usual kinetic law can be written according to Equation 3:

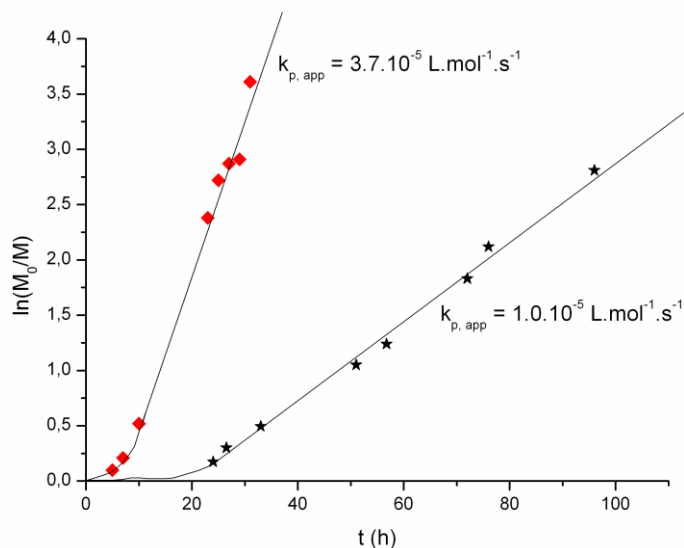
$$- \frac{d[M]}{dt} = k_{app} \cdot [P^*] \cdot [M] \quad \text{equation 3}$$

Where $[M]$ and $[P^*]$ are the concentrations of the monomer and propagating species, respectively. Assuming that the concentration of propagating species is equal to the initial initiator concentration $[I]_0$, Equation 3 can be integrated in Equation 4:

$$\ln \frac{[M]_0}{[M]_t} = k_{app} \cdot [I]_0 \cdot t \quad \text{equation 4}$$

As expected the k_{app} values decreased with temperature, $3.7 \cdot 10^{-5}$ and $1.0 \cdot 10^{-5} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ for 61 and 81°C, respectively. The propagation rate constant for the cationic polymerization of **MOx**

using **GCTs** initiator at 81°C was lower than those obtained with MeOTs and MeI initiators in dimethylacetamide, $240 \cdot 10^{-5}$ and $222 \cdot 10^{-5} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, respectively.[24]



Insert Figure 3.

The cationic ring-opening polymerization of **MOx** initiated by **GCTs** was compared to the polymerization using Solketal® derivative: **Solk-Ts** as summarized in Table 1. The study revealed that the times of polymerization were similar. All obtained polymers were characterized by GPC to determine the molecular weights and the polydispersity indexes. The influence of the temperature on the molecular weight was studied at 61 and 81°C (entries 1 and 2 Table 1). For both initiators the lower values of polydispersity index were reached at 61°C whereas a better control of molecular weights was obtained at 81°C. Therefore a series of POx polymers were synthesized at 81°C with varying $[M]_0/[I]_0$ between 10 and 40 (entries 2-5 Table 1). The molecular weight distribution of the obtained polymer using **GCTs** was close to 1.4 whereas various values were observed in the case of **Solk-Ts**. Moreover **GCTs** initiator offered lower polydispersity index than **Solk-Ts**. In both cases, the experimental

number-average molecular weights measured by GPC analysis were higher than expected M_n . The explanation was the low efficiency of the **GCTs** initiator as mentioned in Figure 1 even if the efficiency of **Solk-Ts** was not investigated in the previous study of Binder et al. One supplementary explanation could be the adsorption of the polymer onto the gels of the GPC columns as already mentioned in the case of polyoxazolines.[25] In addition a plateau appeared when molecular weight attained around 8400 g.mol^{-1} . The plateau could be caused by chain transfer reactions and could explain shoulders which appear in the GPC traces for higher molecular weights (Figure 4).

on

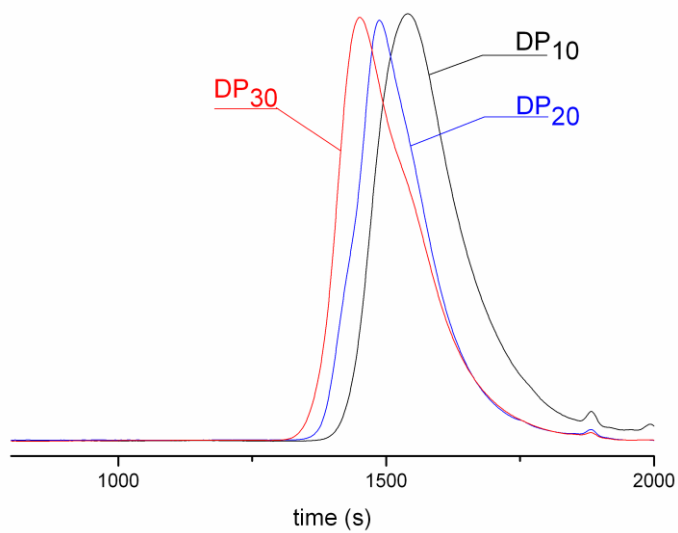
entry	T (°C)	t (h)		yield (%)		\overline{DP}_n			\overline{M}_n			Ip	
		a	b	a	b	a	b	a	b	a	b	a	b
1	61	68	96	52	59	10	60	84	970	5200	7400	1.3 ₄	1.5 ₇

2	81	47	---	89	61	10	48	44	970	4200	4000	1.4 ₉	1.8 ₀
3	81	47	150	83	---	20	76	89	1800	6500	7600	1.4 ₉	1.3 ₄
4	81	47	---	77	---	30	95	---	2700	8100	---	1.4 ₄	---
5	81	47	24	55	34	40	98	48	3500	8400	4400	1.4 ₄	1.6 ₀

^a: our work on **GCTs**.

^b: CROP of **MOx** using **Solk-Ts**. [20]

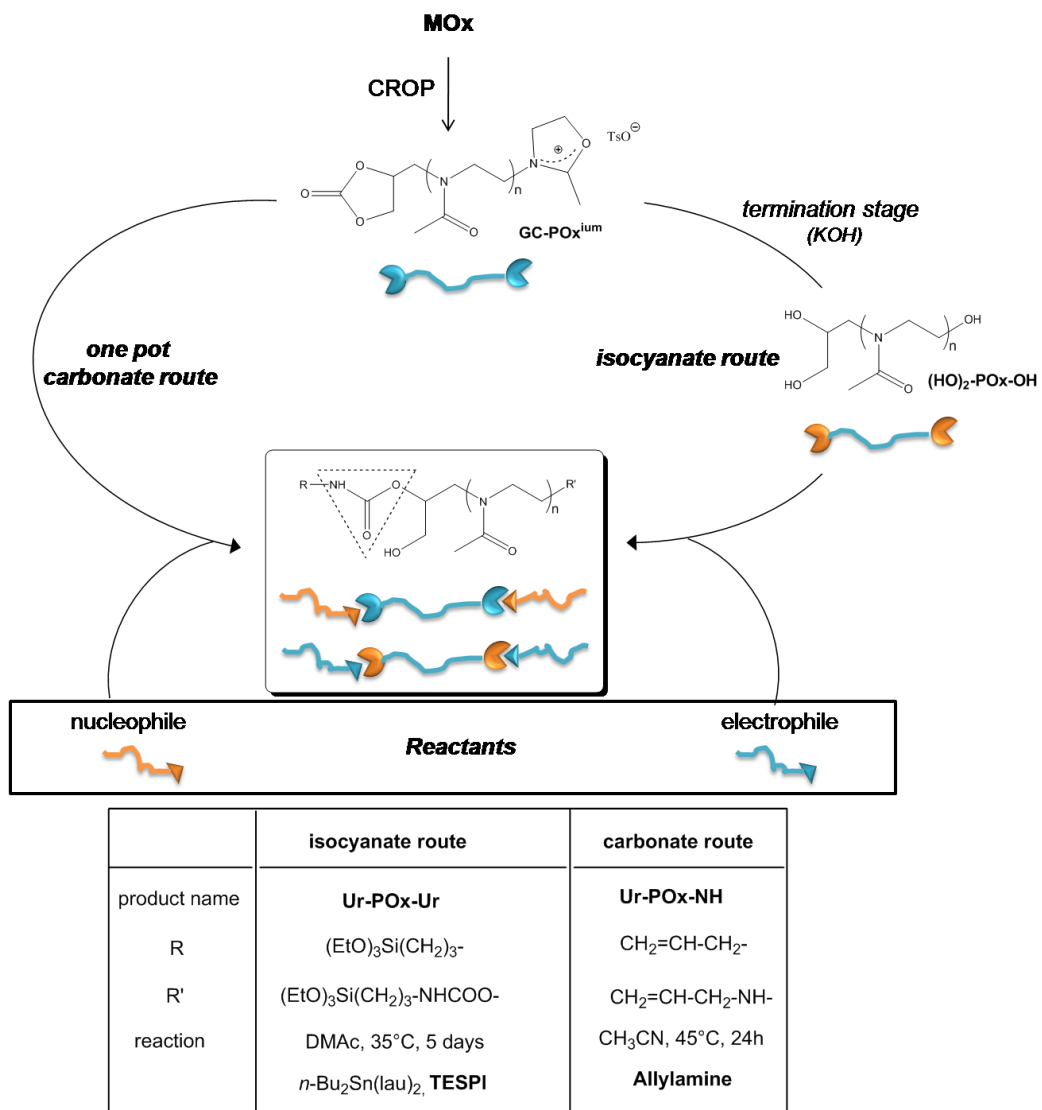
Insert Table 1.



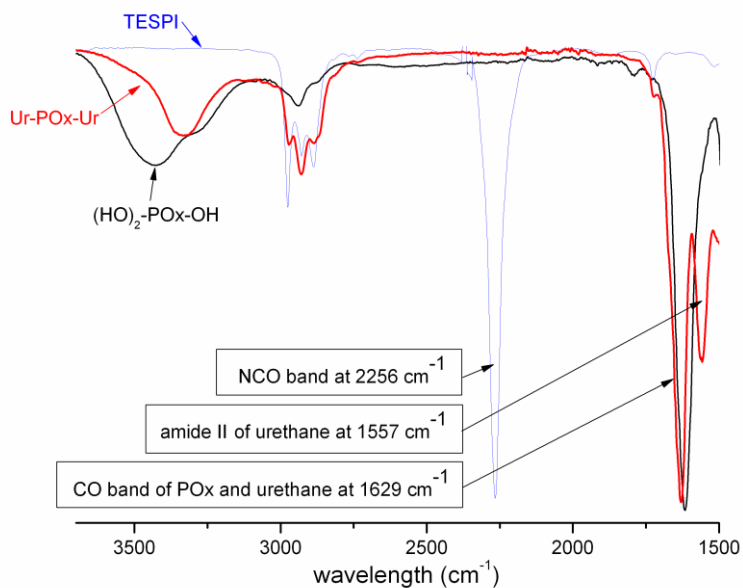
Insert Figure 4.

Simultaneous functionalization of polyoxazoline end chains using isocyanate and carbonate routes

Polyoxazolines bearing carbonate and oxazolinium end chains were converted to telechelic POx according to two alternative routes as described in Scheme 4. The reactive telechelic polymers **GC-POx^{ium}** or **(HO)₂-POx-OH** can act as precursor for functional materials. In this way, polyurethanes are usually prepared from diols and water-sensitive diisocyanates (isocyanate route). In our case **(HO)₂-POx-OH** bearing α -diol and ω -hydroxyl end groups reacted with a peculiar isocyanate: 3-(triethoxysilyl)propyl isocyanate (**TESPI**) (isocyanate route in Scheme 4). **TESPI** provides polymers with the ability to produce organic-inorganic hybrid materials.[26] In the isocyanate route **(Ur-POx-Ur)** polymer was prepared by urethanization of **(HO)₂-POx-OH** with **TESPI** (4.25 equiv with respect to the O-H groups) at 35°C in presence of n-Bu₂Sn(lau)₂. [27] The reaction of urethanization of hydroxyl group can be monitored by FTIR since the large and intense isocyanate band at 2256 cm⁻¹ disappeared on **Ur-POx-Ur** spectrum as evidenced in Figure 5. The large peak assignable to OH bond at 3437 cm⁻¹ also decreased. Moreover the appearance of a peak at 1557 cm⁻¹ proves the formation of urethane groups (H-N-C=O amide II). We noted that carbonyl urethane stretching peak close to 1629 cm⁻¹ overlapped that of polyoxazoline carbonyl one.



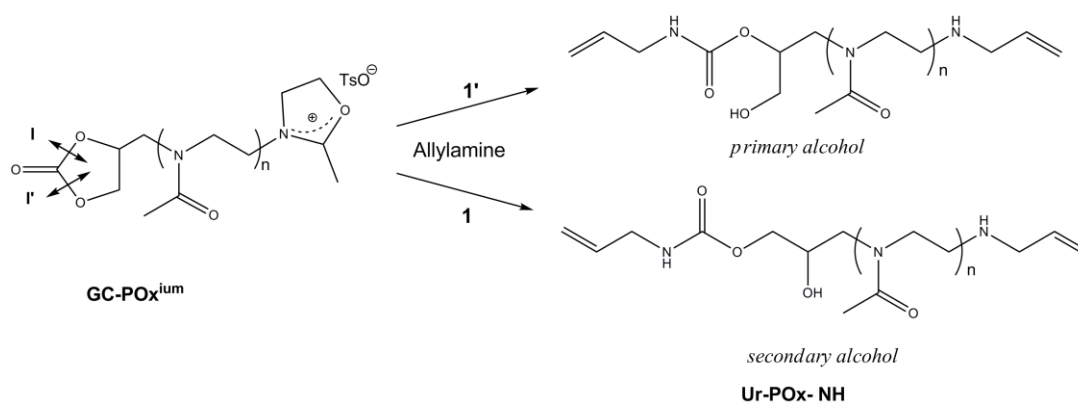
Insert Scheme 4.



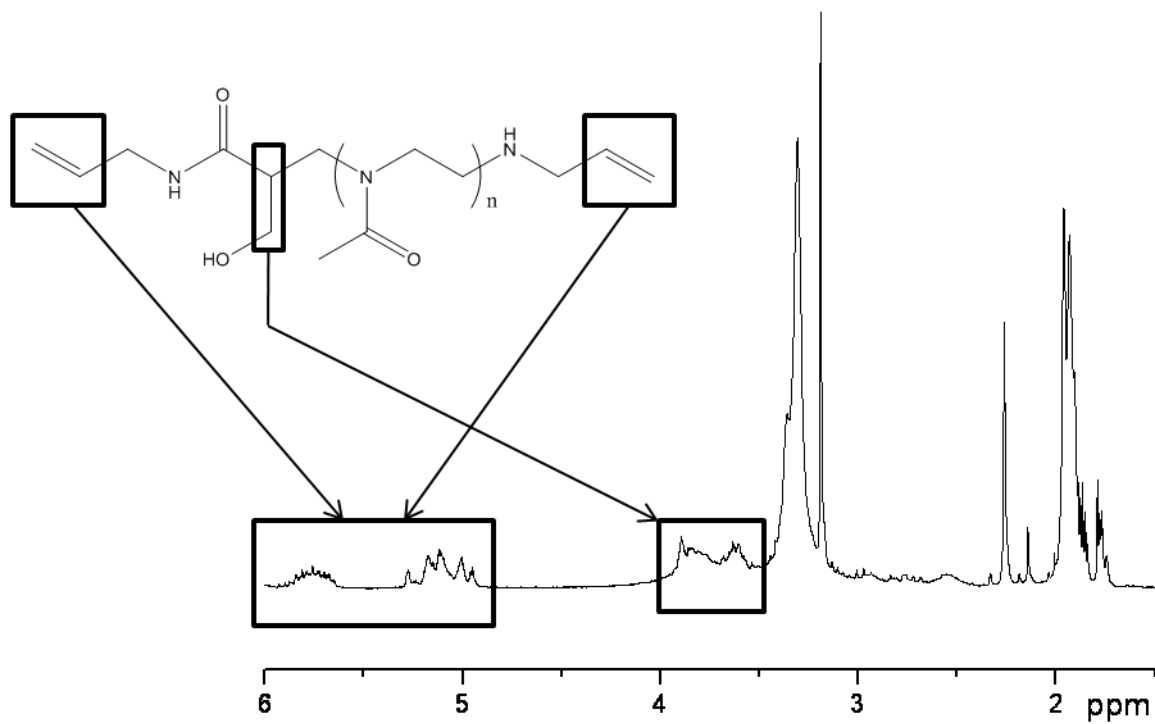
Insert Figure 5.

As an alternative method for preparing urethanes, the chemo-selective reaction of five-membered cyclic carbonate with amine gives urethanes with hydroxyl groups without employing toxic and unstable isocyanates and without catalyst (carbonate route in Scheme 4). The chemo-selective reaction permits the addition of amines on functional carbonate bearing various groups such as alcohol, amide...[28,29] In our case the urethanization has been attempted using **GC-POx^{ium}** and unsaturated amine: allylamine as shown in Scheme 5. One-pot non-isocyanate synthesis of POx bearing urethane group (**Ur-POx-NH**) was realized during the termination stage of the polymerization without preliminary step. Allylamine acted both as terminating agent in the polymerization of **MOx** and reactant with the cyclic carbonate α -end group. In order to determine the best reaction conditions of the termination stage in the presence of allylamine, the polymerization of **MOx** was preliminary realized using MeOTs initiator and gave finally (**Allyl-POx**). The efficiency of the termination agent occurred for 24h at 45°C. Thus at the end of the polymerization of **MOx**, allylamine was added to the reaction mixture containing **GC-POx^{ium}** and the reaction was realized at low

temperature, 45°C, in respect to Endo investigations who studied the reactivity of five-membered cyclic carbonates with amines at low temperature.[30] ^1H NMR spectroscopy analysis confirmed the urethanization of carbonate group and the termination of the polymerization with the presence of typical ethylenic signals at 5.9-5.6 and 5.3-4.9 ppm coming from allylamine end groups on polyoxazoline (Figure 6). According to the carbonate route, non-isocyanate urethane function beared hydroxyl lateral group (Scheme 5). The obtained urethanes show some useful characteristics such as high water absorption because of the existence of hydroxyl groups that cannot be observed in commercial polyurethanes produced by the addition of diisocyanates with diols. As shown in Scheme 5, the reaction of five-membered cyclic carbonates with amines afforded two adducts (1 and 1'), urethanes with primary or secondary hydroxyl groups. In the case of usual carbonates the ratio of the adducts was determined by ^1H NMR integration ratio of the CH_2 protons in α -position to the hydroxyl group. In our case the CH_2 protons of 1 and 1' adducts overlapped in the large peaks at 4.95-3.7 and the ratio of the adducts could not be quantified as already mentioned in the case of aliphatic dicarbonates.[13] Thanks to Scheme 4 we noted the main differences between the two synthetic routes where in the isocyanate route nucleophilic end groups (hydroxyl and diol groups) were reacted with $(\text{HO})_2\text{-POx-OH}$ whereas in the carbonate route electrophilic end groups (carbonate and oxazolium groups) were used with **GC-POx^{ium}**.



Insert Scheme 5.



Insert Figure 6.

Experimental

Materials

Pyridine, TsCl, allylamine, MeOTs, 3-(triethoxysilyl)propyl isocyanate (**TESPI**), di-n-butyltin dilaurate ($n\text{-Bu}_2\text{Sn(lau)}_2$), DMAc, methanol, diethyl ether, CuSO_4 , KOH and CaH_2 were purchased from ACROS and were used as received. 2-Methyl-2-oxazoline (**MOx**) and MeOTs were dried, distilled from CaH_2 and stored under a dry nitrogen atmosphere. Acetonitrile was dried and distilled according to standard procedures.[31] Deuterated solvents (CDCl_3 and CD_3CN) were purchased from SDS and were used without further purification. Glycerol carbonate (**GC**) was a generous gift from ONIDOL Corporation.

Analytical techniques

^1H and ^{13}C NMR spectra were recorded using a Bruker AC 200 with CDCl_3 or CD_3CN as solvent. Size exclusion chromatography was performed on a PL-GPC 50 Plus equipped with an RI refractive index detector. Three PL aquagel-OH columns (25, 7.5 and 4.6 mm ID) were used at 40°C with a $0.8\text{ mL}\cdot\text{min}^{-1}$ flow rate of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$: 7/3 (0.1M LiNO_3), calibrated using POE standards. Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal. Melting points were measured on a Büchi 530 instrument.

4-(p-toluenesulfonate)methyl-1,3-dioxolan-2-one: GCTs

GC (10.09 g, 85.52 mmol) and tosyl chloride (24.46 g, 128 mmol, 1.5 eq) were dissolved in dry acetonitrile (1M). Another acetonitrile solution (1M) containing pyridine (13.53 g, 171 mmol, 2 eq) was prepared. At 5°C the first solution was added dropwise to the second one.

The mixture was stirred for 6 h at room temperature. The reaction mixture was filtered and concentrated under pressure. The resulting product **GCTs** was isolated in 51% yield.

^1H NMR (CDCl_3) δ (ppm): 7.8 (d, 2H, $\text{H}_{\text{aromatic}}$), 7.4 (d, 2H, $\text{H}_{\text{aromatic}}$), 4.9 (m, 1H, $\text{CH}_{\text{cyclic}}$), 4.5 (d, 1H, $\text{CH}_{2\text{cyclic}}$), 4.4 (d, 1H, $\text{CH}_{2\text{cyclic}}$), 4.2 (m, 2H, $\text{CH}_2\text{-SO}_3$), 2.4 (s, 3H, CH_3).

^{13}C NMR (CDCl_3) δ (ppm): 154.2 ($\text{C}=\text{O}$ cyclic), 145.8 ($\text{C}_{\text{aromatic}}\text{-CH}_3$), 131.7 ($\text{C}_{\text{aromatic}}\text{-S}$), 129.9 and 127.5 ($\text{CH}_{\text{aromatic}}$), 73.4 ($\text{CH}_2\text{-SO}_3$), 68.6 ($\text{CH}_{\text{cyclic}}\text{-O}$), 65.2 (CH_2 cyclic), 20.4 (CH_3).

FTIR (cm^{-1}): 2943 (CH), 1796 (C=C), 1635 (C=O), 1425, 1172.

$m_p = 108^\circ\text{C}$.

Typical polymerization of **MOx** using **GCTs**: **(HO)₂-POx-OH**

All reactions were carried out under a dry nitrogen atmosphere. **GCTs** initiator and **MOx** were dissolved in dry acetonitrile (4 M). The solution was vigorously stirred at 81°C for 47h. Then, the product was quenched by addition of KOH-saturated methanolic solution (2.1 eq of KOH). The flask was maintained for 24 h at RT. After cooling, the polymer was isolated by slow precipitation from cold diethyl ether.

^1H NMR (CD_3CN) δ (ppm): 3.9-3.6 (m, 5H, $\text{CH}_2\text{-OH}$, CH-OH and $\text{CH}_2\text{-OH}_{\text{end group}}$), 3.6-3.3 (m, $(4n+2)\text{H}$, CH_2 of POx and $\text{CH}_2\text{-N}$), 2.0 (s, $3n\text{H}$, CH_3 of POx).

^{13}C NMR (CD_3CN) δ (ppm): 171.2-170.6 ($\text{C}=\text{O}$ of POx), CH-OH not observed, 64.9 ($\text{CH}_2\text{-OH}$), 46.2-42.8 (CH_2 of POx and $\text{CH}_2\text{-N}$), 20.9 (CH_3 of POx).

FTIR (cm^{-1}): 3437 (OH), 2936 (CH), 1630 (C=O), 1416, 1175.

Synthesis of **Allyl-POx**

The reaction carried out under a dry nitrogen atmosphere. MeOTs and **MOx** were dissolved in dry acetonitrile (4 M). The solution was vigorously stirred at 81°C . The reaction product was quenched by addition of an adequate amount of allylamine (10 eq). The flask was maintained

for 24 h at 45°C. After cooling, **Allyl-POx** was isolated by slow precipitation from cold diethyl ether. **Allyl-POx** was isolated in 94% yield.

^1H NMR (CDCl_3) δ (ppm): 5.8 (m, 1H, CH=), 5.2 (m, 2H, CH₂=), 3.9-3.3 (m, 4nH, CH₂ of POx), 2.8 (m, 2H, CH₂-N), 2.0 (s, 3nH, CH₃ of POx).

^{13}C NMR (CDCl_3) δ (ppm): 171.2-170.6 (C=O of POx), 132.2 (CH=), 118.1-117.1 (CH₂=), 51.1-43.2 (CH₂ of POx and CH₂-N), 20.9 (CH₃ of POx).

Urethanization of (HO)₂-POx-OH via isocyanate route: Ur-POx-Ur

After the dissolution of **(HO)₂-POx-OH** (0.5121g, 1.42 mmol) in 20 mL of DMAc, **TESPI** (2.2 mL, 6.26 eq) and n-Bu₂Sn(lau)₂ (0.01 mL, 0.012 eq) were added under nitrogen. The reaction was maintained for 5 days at 35°C. **Ur-POx-Ur** was isolated by slow precipitation from cold diethyl ether.

^1H NMR (CD_3CN) δ (ppm): 4.95 (m, 1H, CH-O), 3.6-2.9 (m, (4n+40)H, CH₂ of POx, CH₂-O, CH₂-N and **TESPI**), 2.2-1.95 (s, 3nH, CH₃ of POx), 1.1 (t, 27H, CH₃ of EtOSi).

FTIR (cm^{-1}): 3334 (NH), 2928 (CH), 1629 (C=O of POx), 1557 (C=O amide II of urethane).

Urethanization of GC-POx^{ium} via carbonate route: Ur-POx-NH

GCTs initiator and **MOx** were dissolved in dry acetonitrile (4 M). The solution was vigorously stirred at 81°C. The reaction product **GC-POx^{ium}** was quenched by addition of an adequate amount of allylamine (10 eq). The flask was maintained for 24 h at 45°C. After cooling, the polymer was isolated by slow precipitation from cold diethyl ether. **Ur-POx-NH** was isolated in 61% yield.

^1H NMR (CD_3CN) δ (ppm): 5.9-5.6 (m, 2H, CH=), 5.3-4.9 (m, 4H, CH₂=), 3.9-3.5 (m, 3H, CH₂-OH, CH-OH and CH-OCONH), 3.5-3.2 (m, (4n+6)H, CH₂ of POx, CH₂-CH= and CH₂-NCOMe), 2.0-1.6 (s, 3nH, CH₃ of POx).

Conclusion

This study showed that **GCTs** coming from glycerol carbonate could act as functional initiator in the cationic ring-opening polymerization of oxazoline. The synthesis of polyoxazoline **GC-POx^{ium}** carrying α -carbonate group and ω -oxazolium group was reported. The carbonate head group could be converted into diol with KOH addition to give **(HO)₂-POx-OH**. Thus in situ polymerization and functionalization occurred. The comparison of two bio-based initiators coming from glycerol **GCTs** and **Solk-Ts** showed that **GCTs** offered the narrowest polydispersity and a better control of molecular weight even if its partial efficiency in the initiation step was demonstrated. Then the chemical modification of the end chains of polyoxazoline by urethanization was achieved using two alternative routes. In the isocyanate route the urethanization of hydroxyl end groups of **(HO)₂-POx-OH** with functional isocyanate **TESPI** was checked by FTIR spectroscopy. In the carbonate route the reaction of nucleophiles as amines with carbonate and oxazolium end chains of **GC-POx^{ium}** occurred in the same time as evidenced in NMR study. This work demonstrated that the functional initiator **GCTs** could be used to generate α,ω -functionalized polyoxazolines. This method is versatile and can accept many nucleophiles compatible with carbonate chemistry and many electrophiles compatible with isocyanate chemistry.

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References

- [1] Adams N., Schubert U. S. *Adv. Drug Delivery Rev.* **2007**, 59, 1504-1520.
- [2] Woodle M. C., Engbers C. M., Zalipsky S. *Bioconjugate Chemistry* **1994**, 6, 493-496.
- [3] Kobayashi S. *Progress in Polymer Science* **1990**, 15, 751-760.
- [4] Giardi C., Lapinte V., Charnay C., Robin J. J. *React. Funct. Polym.* **2009**, 69, 643-649.
- [5] Biermann U., Friedt W., Lang S., Luhs W., Machmuller G., Metzger J. O., Klaas M. R., Schafer H. J., Schneider M. P. *Angew. Chem., Int. Ed. Engl.* **2000**, 39, 2206-2224.
- [6] Jenck J. F., Agterberg F., Droscher M. J. *Green Chem.* **2004**, 6, 544-556.
- [7] Zheng Y., Chen X., Shen Y. *Chem. Rev.* **2008**, 108, 5253-5277.
- [8] Corma A., Iborra S., Velty A. *Chem. Rev.* **2007**, 107, 2400-2502.
- [9] Rokicki G., Rakoczy P., Parzuchowski P. G., Sobiecki M. *Green Chem.* **2005**, 7, 529-539.
- [10] Parzuchowski P. G., Jaroch M., Tryznowski M., Rokicki G. *Macromolecules* **2008**, 41, 3859-3865.
- [11] Wolfson A., Dlugy C., Shotland Y. *Environ. Chem. Lett.* **2007**, 5, 67-71.
- [12] Simao A. C., Lynikaite-Pukleviciene B., Rousseau C., Tatibouet A., Cassel S., Sackus A., Rauter A. P., Rollin P. *Lett. Org. Chem.* **2006**, 3, 10, 744-748.
- [13] Tomita H., Sanda F., Endo T. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, 39, 3678-3685.
- [14] PCT Patent 107568 2008.
- [15] UK Patent 2432160 2007.
- [16] Fricke N., Keul H., Möller M. *Macromol. Chem. Phys.* **2009**, 210, 242-255.
- [17] Rousseau J., Rousseau C., Lynikaité B., Sackus A., De Leon C., Rollin P., Tatibuët A. *Tetrahedron*, **2009**, 65, 8571-8581.
- [18] Shaikh A. A. G., Sivaram S. *Chem. Rev.* **1996**, 96, 951-976.
- [19] Clements J. H. *Ind. Eng. Chem. Res.* **2003**, 42, 663-674.

- [20] Einzmann M., Binder W. H. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, 39, 2821.
- [21] Brissault B., Guis C., Cheradame H. *Eur. Polym. J.* **2002**, 38, 219-228.
- [22] Saegusa T., Ikeda H. *Macromolecules* **1973**, 6, 808-811.
- [23] Matyjaszewski K., Cationic polymerizations: mechanisms, synthesis, and applications, Marcel Dekker Inc., New York, 1996.
- [24] Hoogenboom R., Fijten M. W. M., Schubert U. S. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, 42, 1830-1840.
- [25] Hoogenboom R., Paulus R. M., Fijten M. W. M., Schubert U. S. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, 43, 1487-1497.
- [26] Sakka S., Handbook of Sol-Gel Science and Technology: Processing, Characterization and Applications, V. I - Sol-Gel Processing , Kluwer Academic Publishers, **2005**.
- [27] Pardal F., Lapinte V., Robin J.J. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, 47, 4617-4628.
- [28] Ochiai B., Satoh Y., Endo T. *Green Chem.* **2005**, 7, 765-767.
- [29] Ochiai B., Inoue S., Endo T. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, 43, 6613-6618.
- [30] Tomita H., Sanda F., Endo T. *J. Polym. Sc. Part A Polym. Chem.* **2001**, 39, 4091-4100.
- [31] Perrin. D., Purification of laboratory chemicals. New york: Pergamon press, 1980.

Table captions

Table 1. Characterization data for CROP of **MO_x** using **Solk-Ts** and **GCTs** initiators.

Figure captions

Figure 1. Study of the initiation stage by ¹H NMR analysis in CDCl₃ (*: residual CHCl₃).

Figure 2. Evolution of conversion versus time of polymerization using **GCTs** at 61 and 81°C.

Figure 3. Ln([M]₀/[M]) versus reaction time for **MO_x** using **GCTs** (♦81°C, ★61°C).

Figure 4. GPC traces of various lengths of **(HO)₂-PO_x-OH** chain.

Figure 5. FTIR spectra of **TESPI**, **(HO)₂-PO_x-OH** and **Ur-PO_x-Ur**.

Figure 6. ¹H NMR spectrum of **Ur-PO_x-NH** in CDCl₃.

Graphical

The synthesis of polyoxazoline has been achieved via cationic ring-opening polymerization of 2-methyl-2-oxazoline using glycerol carbonate derivative as bio-based initiator. The article focuses on end group modifications using isocyanate and carbonate routes.

