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Fatty Acid-Based Polycarbonates Synthesis and Crosslinking Through the Malonate Route

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In this study, a series of fatty acid-based 6-member cyclic carbonates, 6CCs, were synthesized through the malonate route and the conditions to their copolymerization with trimethylene carbonate (TMC) optimized. These functional aliphatic polycarbonates were fully characterized and the influence of several parameters on the polymer properties investigated. Finally, preliminary experiments of the derivation and crosslinking of these polycarbonates were carried out.

Introduction

Aliphatic polycarbonates are well known for their specific features such as low T_g , resistance towards hydrolysis, biocompatibility and biodegradability. Their synthesis can be achieved *via* different routes but they are mainly synthesized through ring-opening polymerization (ROP) of cyclic carbonate monomers.¹ Indeed, under suitable conditions, the ROP of cyclic carbonates affords the polymer in a controlled manner. In addition to the molar mass and dispersity, the polymer microstructure and the nature of end-groups can be controlled.

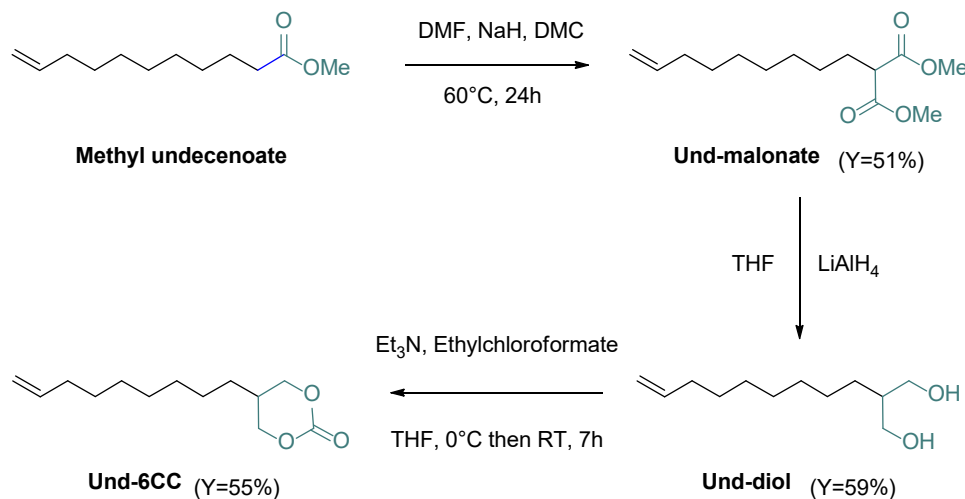
The advantage of functional polycarbonates over the traditional poly(trimethylene carbonate), PTMC, is the possibility to modulate the polymer physico-chemical properties to specific needs, thereby broadening and improving their performance characteristics. Such functional polymers can be synthesized either upon direct polymerization of the functionalized monomer or upon chemical modification post-polymerization.

Moreover, because of environmental concerns and also in view of fossil fuel depletion, the use of building blocks from renewable resources such as vegetable oils, terpenes or sugars is of great interest.² With this philosophy, we aimed at synthesizing a platform of fatty acid-based cyclic carbonates as precursors of original aliphatic bio-based polycarbonates. For this purpose, we investigated the design of vegetable oil-based 6-membered cyclic carbonates (6CCs) from bio-sourced methyl undecenoate.³⁻⁷

In this context, the synthesis of a series of bio-based 6CCs through the formation of a malonate intermediate was investigated and the experimental conditions to polymerize these cyclic carbonates, optimized. These functional aliphatic polycarbonates were then fully characterized by NMR, SEC, DSC and TGA and the influence of several parameters on the polymer properties was also investigated. Finally, preliminary experiments of the derivation and crosslinking of such polymers have been conducted.

Synthesis of Bio-Based 6-Membered Cyclic Carbonates

As illustrated in Scheme 1, a 6-membered ring cyclic carbonate bearing unsaturation moiety was prepared from fatty-acid derivatives using a three-step procedure.³ The Figure 1 presents the stacked ¹H NMR spectra of the different intermediates starting from methyl undecenoate.



Scheme 1. Synthetic route to functional 6-membered cyclic carbonate from methyl undecenoate.³

The first step consisted in the malonate synthesis at 60°C for 24 hours from methyl undecenoate using 40 equivalents (equiv.) of dimethyl carbonate (DMC, acting also as a solvent), 2.5 equiv. of NaH and 1 equiv. of DMF. This approach using the non-toxic DMC rather than phosgene and its derivatives was developed by Kolb *et al.*^{8,9} The authors proved that a large excess of DMC prevents Claisen-condensation side product. This method has been optimized by Maisonneuve *et al.*³ who performed the synthesis of **Und-6CC** for the synthesis of poly(hydroxyurethane)s. Additionally, anhydrous DMF can accelerate considerably the deprotonation in α -position of the ester by increasing the solvation of the reactants and/or the intermediates. The conversion of methyl undecenoate into **Und-malonate** was confirmed by ¹H NMR spectroscopy. The signal at 3.66 ppm of the methylene protons nearby the ester linkage of methyl undecenoate has disappeared (See Figure 1-(1)). In addition, a triplet at 3.35 ppm and a multiplet at 1.88 ppm, corresponding to the malonate group protons, confirmed the synthesis of **Und-malonate**.

In a second step, the reduction of **Und-malonate** was carried out using 4.1 equiv. of LiAlH₄ as reducing agent. The synthesis of the corresponding diol (**Und-1,3-diol**) was confirmed by ¹H NMR (See Figure 1-(3)) with the disappearance of the singlet and the triplet at 3.73 ppm and 3.35 ppm respectively, combined with the appearance of the two multiplets at 3.78 ppm and 3.63 ppm assigned to the methylene protons nearby the hydroxyl groups.

In the literature, various methods have been developed to cyclize 1,3-diols to form 6-membered cyclic carbonates.¹⁰⁻¹⁶ One of these methods involves the use of ethyl chloroformate and triethylamine (TEA). To obtain **Und-6CC** from the cyclization of **Und-1,3-diol**, this method was preferred over non phosgene route due to the compared high conversion obtained. The structure of the 6-membered cyclic carbonate was confirmed by ¹H NMR (See Figure 1-(4)). The spectrum clearly shows the disappearance of the two multiplets corresponding to the methylene protons nearby the hydroxyl groups and the appearance of the two multiplets at 4.10 ppm and 4.35 ppm assigned to the cyclic carbonate protons. However, due to the multiple steps, the overall yield of this synthesis was approximately equal to 13 % with methyl undecenoate as starting reagent.

Using the same procedure, a series of bio-based cyclic carbonates were synthesized from other fatty acid derivatives. The latter are depicted in Figure 2 and their detailed syntheses are given in the experimental part. The yields of these syntheses were similar than the one for the synthesis of **Und-6CC**.

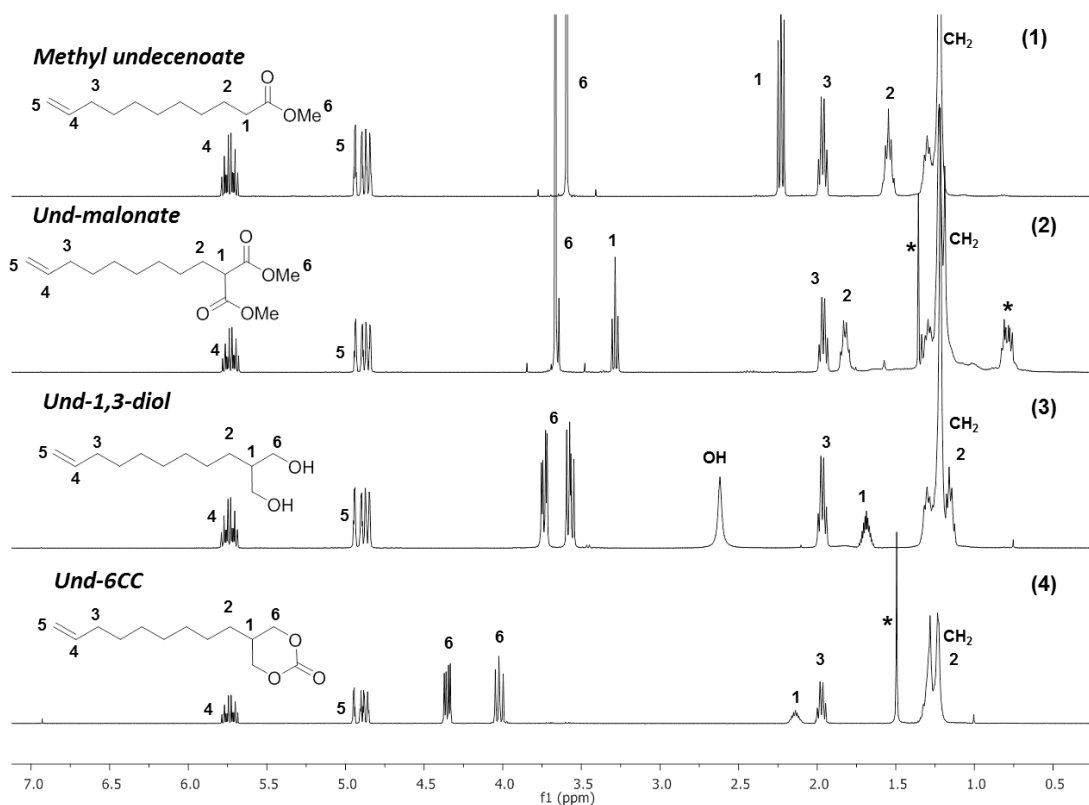


Figure 1. Stacked ¹H NMR spectra of (1) methyl undecenoate, (2) Und-malonate, (3) Und-1,3-diol and (4) Und-6CC. (All analyses were performed in CDCl₃) (*: residual solvents).

This first platform (Figure 2) allowed us to study the effect of different parameters on the polycarbonate synthesis. The influence of the chain length as well as of the number of unsaturations was investigated by synthesizing **Ole-6CC** from methyl oleate and **Lin-6CC** from methyl linoleate, respectively. Lastly, **Ric-6CC** from methyl ricinoleate was prepared in order to evaluate the effect of the polar hydroxyl group. Based on several studies,^{17–19} an hydroxyl group was introduced on the cyclic carbonate side chain to bring polarity (**Ric-6CC**). The synthesis is detailed in the experimental part. The hydroxyl group could be useful for further post-modification reactions even though it requires protection prior to the polymerization due to its incompatibility with the ring-opening process. Hydroxyl functional groups have been commonly introduced into biodegradable polymers *via* homopolymerization of benzyloxy^{20–22} or acetal^{23–26} protected cyclic carbonate followed by deprotection with Pd/C or hydrolysis in mild acidic conditions.

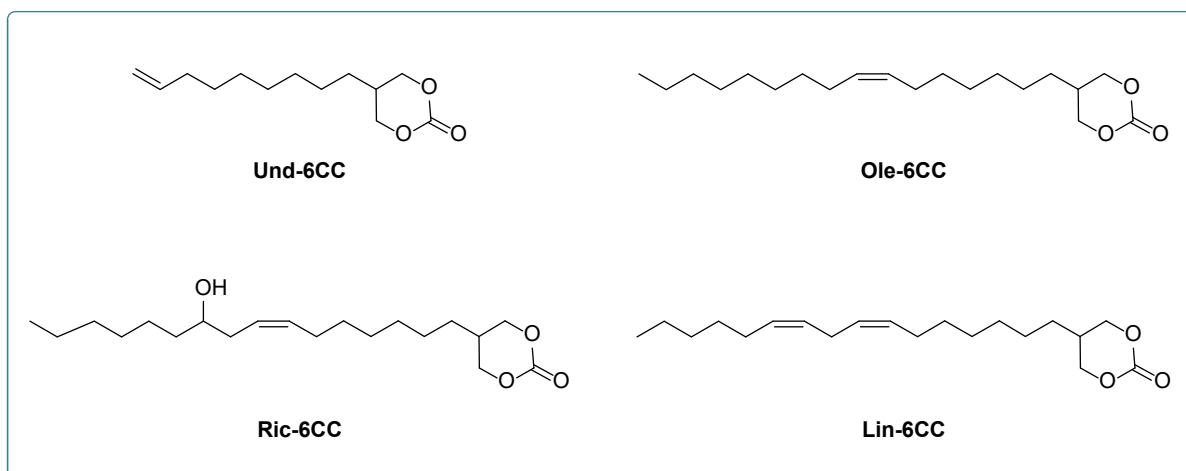
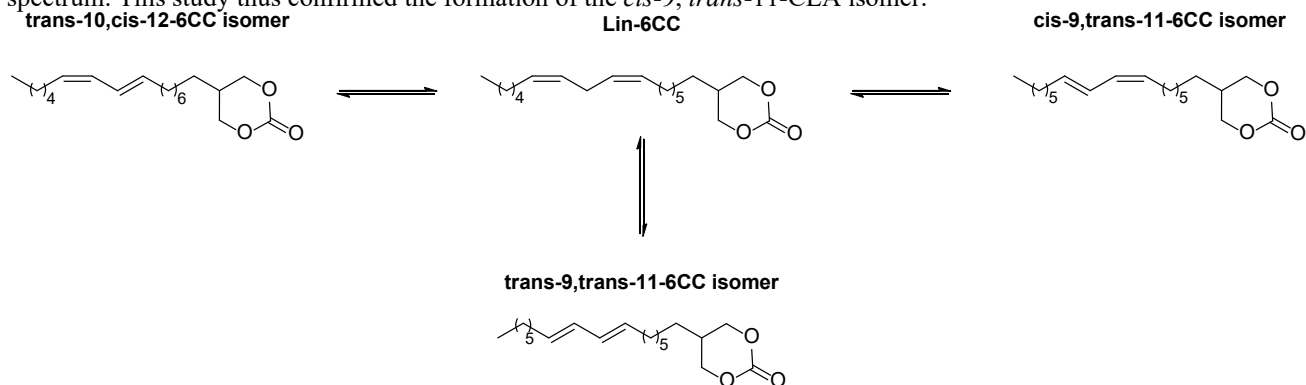


Figure 2. First platform of fatty acid-based 6-membered cyclic carbonates.

All these structures were confirmed by ^1H NMR analyses (*Figure 3). For **Ole-6CC**, a unique signal in the vinylic region at 5.33 ppm confirmed the presence of an internal double bond. Concerning **Lin-6CC**, ^1H NMR spectrum shows weak signals at 6.26 ppm, 5.95 ppm and 5.63 ppm, respectively. These signals are assigned to protons belonging to isomerized methyl linoleate derivatives. Indeed, Jie *et al.*^{27,28} highlights the isomerization of linoleic acid into *trans*-9,*trans*-11-conjugated linoleic acid (CLA), *trans*-10,*cis*-12-CLA and *cis*-9,*trans*-11-CLA as illustrated in Scheme 2. Moreover, Gunstone and Said²⁹ noted that the presence of DBU in a reaction media appeared to be very suitable for the preparation of the *cis*-9, *trans*-11-CLA isomer. Unsurprisingly, characteristic signals of this latter isomer observed by ^1H NMR fit with the unassigned signals in the **Lin-6CC** ^1H NMR spectrum. This study thus confirmed the formation of the *cis*-9, *trans*-11-CLA isomer.



Scheme 2. Isomerization reactions of **Lin-6CC**.

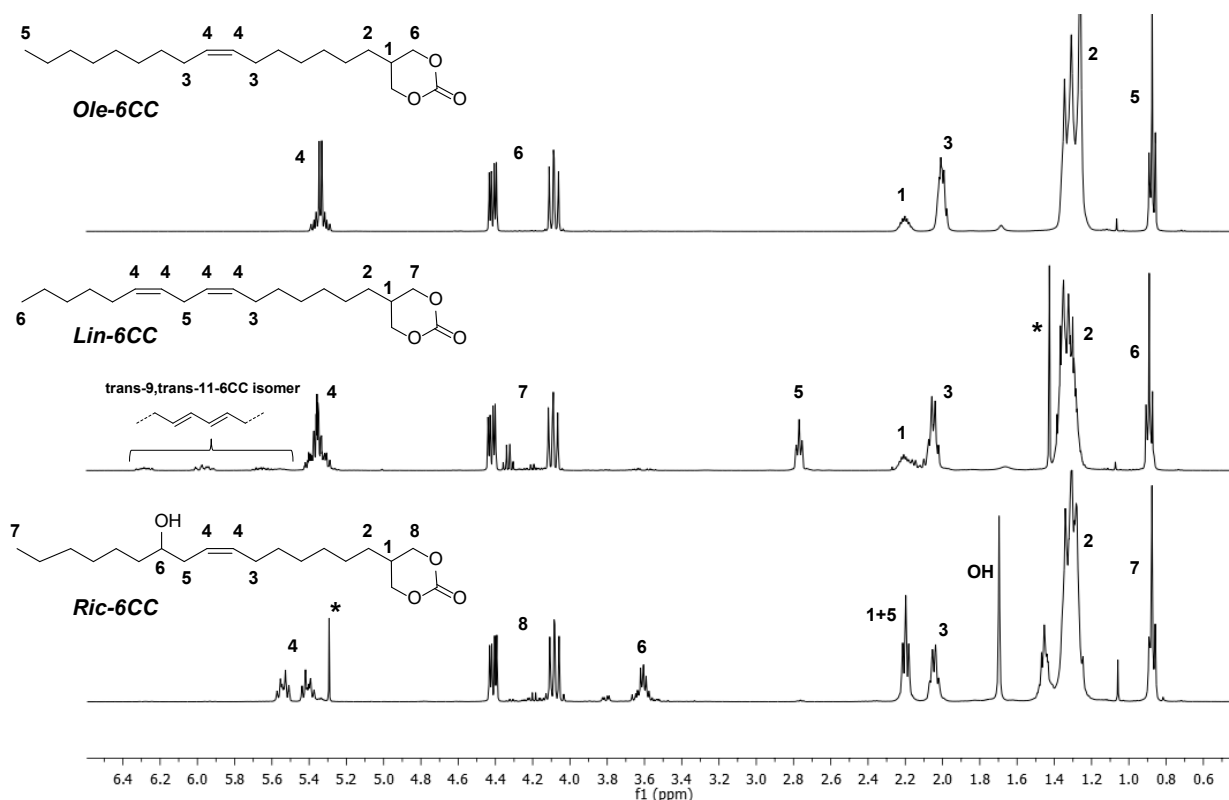


Figure 3. Stacked ^1H NMR of **Ole-6CC**, **Lin-6CC** and **Ric-6CC** in CDCl_3 .

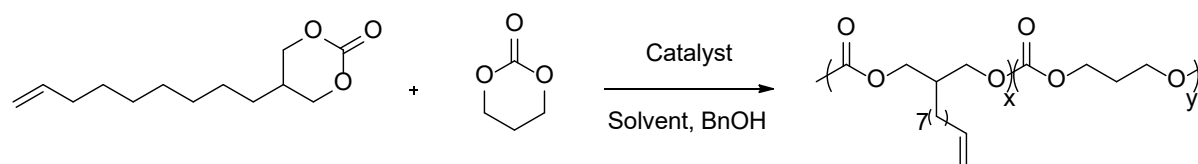
To conclude this part, four different fatty acid-based 6CCs were synthesized using the malonate route. All these cyclic carbonates were liquid but highly viscous at room temperature, which is not very convenient for polymerization purposes. The 6CC syntheses were scaled-up to maximum 3 grams starting from 20 grams of fatty acid. This synthetic pathway to 6CCs shows some limitations such as a rather overall low yield (around 10%) and a tedious work-up, for instance, with the treatment of large quantities of sensitive reactants such as NaH and LiAlH_4 .

Ring-Opening Polymerization of the Bio-Based 6CC

A wide variety of methods are available for the polymerization of six-membered cyclic carbonates. The first approach involves the use of an organometallic weak Lewis acid catalyst, $\text{Sn}(\text{Oct})_2$, known to be an active complexation catalyst for the polymerization of cyclic carbonates.^{20–22,25,30–51} $\text{Sn}(\text{Oct})_2$ is a widely used catalyst for the synthesis of polyesters and polycarbonates for biomedical applications due to its acceptance by the United States Food and Drug Administration as a food additive. The second route to polycarbonates deals with the organo-catalyzed ROP of 6CCs. Indeed, organo-catalysts have been widely investigated towards the polymerization of cyclic monomers such as carbonates and lactones.^{52,53} This type of catalysis present the advantage not to use toxic heavy metals, which are most of the time difficult to completely remove from the polymers. Among the catalytic systems, the amidine 1,8-diazabicycloundec-7-ene (DBU) associated with a thiourea has been extensively used for the polymerization of cyclic carbonates (**MAC**, **MBC**, **MPC**,...) ^{5,41,47,54–71} enabling a control over molar masses, dispersity and functional end-groups of the resulting polymers. Bio-based cyclic carbonates (see Figure 2) were first copolymerized with TMC, as illustrated in Table 1. Different parameters were investigated such as the nature of the catalyst, the influence of the monomer ratios and the effect of the copolymer composition on the thermal properties.

The random copolymerizations of **Und-6CC** and TMC were first carried out in toluene at 120°C or in THF at 60°C ($[\text{Und-6CC}]_0 + [\text{TMC}]_0 = 4 \text{ mol.L}^{-1}$) using several catalysts (Figure 4) and benzyl alcohol as initiator with $[\text{Und-6CC}]_0 / [\text{TMC}]_0 / [\text{Catalyst}]_0 / [\text{BnOH}]_0$ ratios of 10:90:1:1 in a perfectly homogeneous solution. Benzyl alcohol added as co-initiator accelerated the polymerization process and afforded a better control of the molar mass by monitoring the monomer/co-initiator ratio. The **Und-6CC** to TMC ratio was kept equal to 10/90 because **Und-6CC** was suspected to be less reactive in ROP due to its long pendant alkyl chain. The polymerizations were performed in gram scale until full conversion of TMC. Free monomers were removed by precipitating out the polymer in cold methanol (Yield = 80-85 % calculated with the ratio: g of precipitated copolymer/g of the monomers). All the results are summarized in Table 1.

Table 1. Catalysts Screening for the Copolymerization of Und-6CC and TMC^a



Entry	Catalyst (1 mol.%)	Solvent/T	Und-6CC content (%) ^b	Reaction duration to full conversion of TMC (hours)	M_n^c (g.mol ⁻¹)	\mathcal{D}^c
1	TBD	THF/60°C	8.2	72	4 200	1.41
2	DBU	THF/60°C	9.0	144	3 200	1.35
3	NHC-IPr	THF/60°C	0	2	12 000	1.95
4	$\text{Sn}(\text{Oct})_2$	Toluene/120°C	9.1	5	5 400	1.49

^areaction conditions: 10 equiv. of Und-6CC, 90 equiv. of TMC, 1 equiv. of BnOH, 1 equiv. of catalyst; ^bCalculated from ¹H NMR spectra; ^cDetermined by SEC with polystyrene standards.

Catalysts:

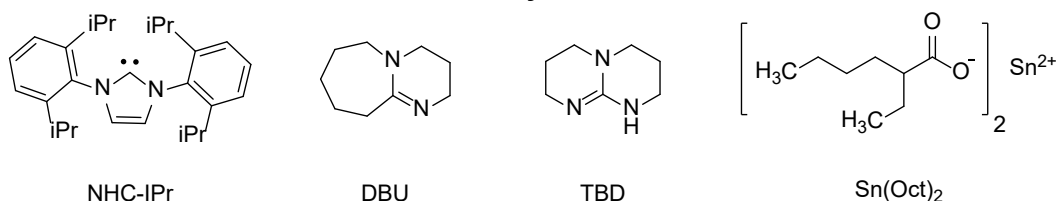


Figure 4. Catalysts used during the copolymerization of Und-6CC and TMC.

Und-6CC unit content was calculated from the integration of characteristic signals of both monomer units (Equation 1).

$$\text{Und} - 6\text{CC content (\%)} = \frac{\int H_{\text{Und-6CC}} (H_2)}{\int H_{\text{Und-6CC}} (H_2) + \int H_{\text{TMC}} (H_6)}$$

Equation 1. Formula used for the calculation of Und-6CC units incorporated in the copolymer.

For all experiments, ^1H NMR showed that characteristic signals of both TMC units ($\delta = 4.17$ and 1.98 ppm) and **Und-6CC** units ($\delta = 5.75$, 4.89 and 4.07 ppm) were clearly detected (Figure 5). The singlet at 5.09 ppm was assigned to the methylene protons on the benzyl alcohol acting as the polymerization initiator. It is important to note that no signals were observed between 3.3 and 3.7 ppm corresponding to ether signals. Thus, no decarboxylation side reaction occurred during the polymerization.

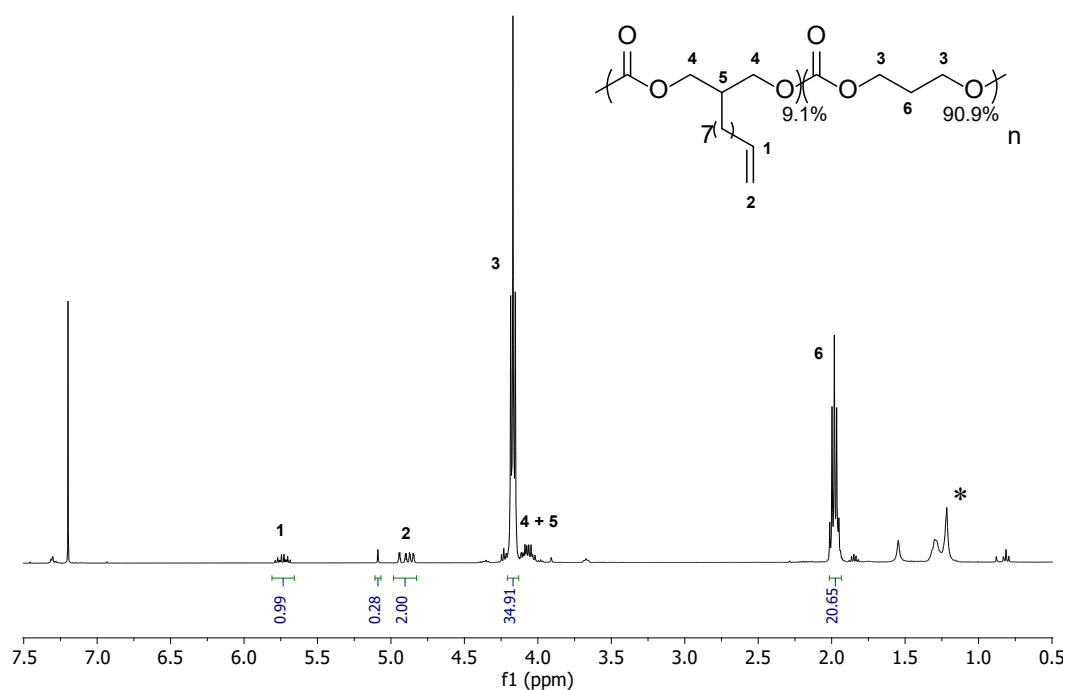


Figure 5. ^1H NMR spectrum of $P(\text{TMC-co-Und-6CC})$ (Table 1, entry 4) (*: CH_2 signals of Und-6CC units).

The highest incorporation of **Und-6CC** monomer was obtained with $\text{Sn}(\text{Oct})_2$ (entry 4), reaching 9.1%. As a general trend, the obtained copolymers exhibited moderate molar masses with unimodal distribution and a relative narrow dispersity (see Figure 6).

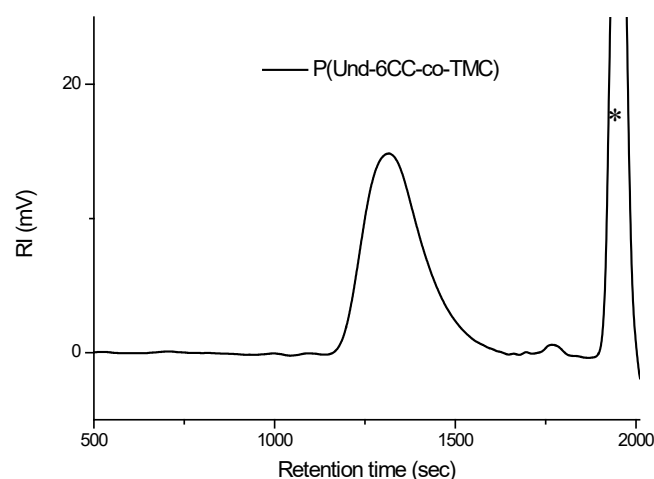
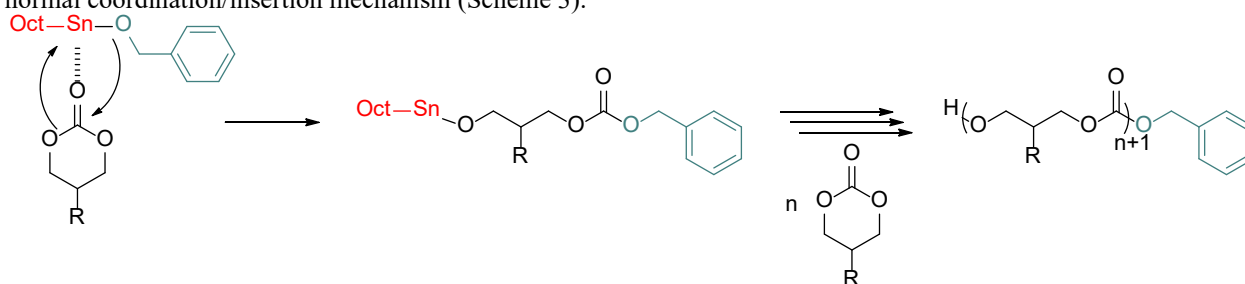


Figure 6. Typical SEC trace in THF of P(Und-6CC-co-TMC) (Table 1, entry 4) (*: Flow marker).

The ring-opening polymerization mechanism of TMC using $\text{Sn}(\text{Oct})_2$ was investigated by Kricheldorf and coll..⁴⁶ Besides, benzyl alcohol undergoes a rapid complexation and equilibration reaction with $\text{Sn}(\text{Oct})_2$. The authors demonstrated that below 120°C , the resulting tin benzyloxy group initiated the polymerization of TMC via the normal coordination/insertion mechanism (Scheme 3).

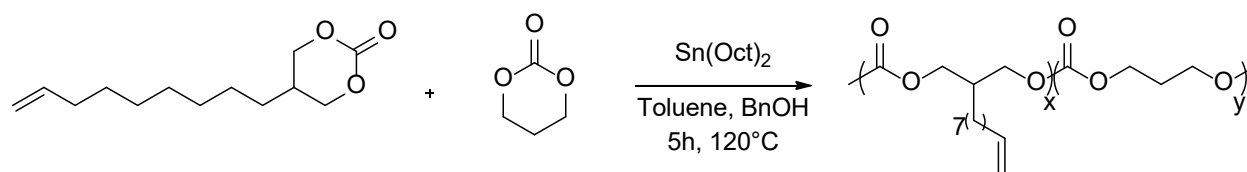


Scheme 3. ROP mechanism of cyclic carbonate initiated by benzyl alcohol and $\text{Sn}(\text{Oct})_2$.

Surprisingly, when the polymerization was performed with 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**NHC-IPr** in Table 1) as a catalyst, no incorporation of **Und-6CC** monomer was observed. This is presumably due to the too high activity of the carbene towards TMC in comparison to less reactive **Und-6CC**. Interestingly, in the presence of TBD or DBU as organo-catalysts (entry 1 and 2), a relatively good control of the polymerization was achieved. Indeed, 8.2 mol.% and 9.0 mol.% (out of 10 mol.% maximum) of **Und-6CC** was respectively incorporated in the resulting polycarbonate, with reasonable dispersity (1.41 and 1.35 respectively). However, the inconvenient to work with these systems is the long reaction time. While the polymerization lasts for 5 hours using $\text{Sn}(\text{Oct})_2$ as catalyst, it takes 3 days with TBD and 6 days with DBU. Finally, for all above-mentioned features, $\text{Sn}(\text{Oct})_2$ was chosen as catalyst for further polymerizations.

The influence of the co-monomers ratio was then investigated on the resulting copolymer composition. A series of different copolymers and homopolymers were prepared from **Und-6CC** and TMC as summarized in Table 2. The copolymerizations were performed with $\text{Sn}(\text{Oct})_2$ as catalyst (1 mol.% with respect to **Und-6CC** + TMC) and BnOH as initiator (also 1 mol.% with respect to **Und-6CC** + TMC) at 120°C in toluene for 5 hours ($[\text{Und-6CC}]_0 + [\text{TMC}]_0 = 4 \text{ mol.L}^{-1}$). Due to the poor reactivity of **Und-6CC**, its homopolymerization producing P(**Und-6CC**) was performed during 48h.

In order to purify the (co)polymers, free monomers were removed by precipitating out the polymer in cold methanol. Copolymers were obtained as viscous oils. The yield of the polymerization was calculated by the ratio of g. of precipitated copolymer vs g. of monomers.

Table 2. Ring-Opening (Co)polymerization of Und-6CC with TMC with Different Co-Monomer Ratios^a

Entry	Und-6CC/ TMC molar feed ratio	Conversion Und-6CC (%) ^b	Und-6CC incorporation (%) ^b	Yield (%)	M_n ($\text{g}\cdot\text{mol}^{-1}$) ^c	$[\text{D}]$ ^c	T_g ^d (°C)	T_d (°C) ^e
P(Und-6CC)	100/0	100	100	13	2 500	1.25	-60.8	218
P2	50/50	83	34	35	1 800	1.37	-65.8	180
P3	10/90	73*	9.1	72	5 400	1.49	-34.1	206
P4	5/95	nd*	3.9	88	7 400	1.53	-26.1	203
PTMC	0/100		0	90	53 000	1.48	-19.3	196

^areaction conditions: 1 mol % of BnOH, 1 mol % of Sn(Oct)₂, 120°C, 5h; ^bCalculated from ¹H NMR spectra; ^cEstimated by SEC with polystyrene standards; ^dMeasured from the second heating run of DSC; ^eDetermined by TGA at 10°C·min⁻¹ under nitrogen after 5 wt.% loss. *: could not be determined due to overlapping of the ¹³C satellite peak of proton 3 at 4.17 ppm with the residual proton 6 of unreacted Und-6CC at 4.35 ppm.

Und-6CC unit content was calculated from the integration of characteristic signals of both monomer units (Equation 1). The results showed that P(Und-6CC-co-TMC) copolymers were obtained with Und-6CC contents ranging from 3.9 to 34 mol.%, Und-6CC feed ratio varying from 5 to 50 mol.% with respect to TMC. Since Und-6CC is less reactive in ROP, its incorporation in the copolymer is close to the one predicted only for low Und-6CC feed ratio. Indeed, for 10 mol.% and 5 mol.% (entries P3 and P4, Table 2) of Und-6CC, the composition of the copolymer is in relative good agreement with the feed ratio. For higher lipidic monomer feed ratio, the amount of Und-6CC incorporated in the copolymer is lower than the expected value. For example, only 34 mol.% of Und-6CC was incorporated in the copolymer whereas 50 mol.% was present in monomer feed (entry P2, Table 2). The lack of reactivity of the fatty acid-based monomer in comparison with TMC is presumably the reason of this difference.

In addition, an increase of Und-6CC content in the copolymer is associated with a decrease in molar mass. Indeed, under the same polymerization conditions, the polymer molar mass dropped significantly (from 53 000 $\text{g}\cdot\text{mol}^{-1}$ to 7 400 $\text{g}\cdot\text{mol}^{-1}$) when 5 mol.% of functional bio-based units was incorporated into PTMC backbone. Similarly, the yield of polymerization decreases as a function of the bio-based monomer content. Due to the difficulty of Und-6CC to undergo ROP, the yield of its homopolymerization is only 15%.

The thermal properties of the copolymers were evaluated by DSC (see Figure 7). As expected, all the random copolymers are amorphous and exhibit only one T_g . The presence of Und-6CC units bringing long pendant alkyl chains lowers the T_g values. The latter range from -19.2 °C for PTMC to -60.8 °C for P(Und-6CC). The lowest T_g of -65.8°C exhibited by the copolymer with 34 mol.% of Und-6CC units was reflecting the copolymer composition.

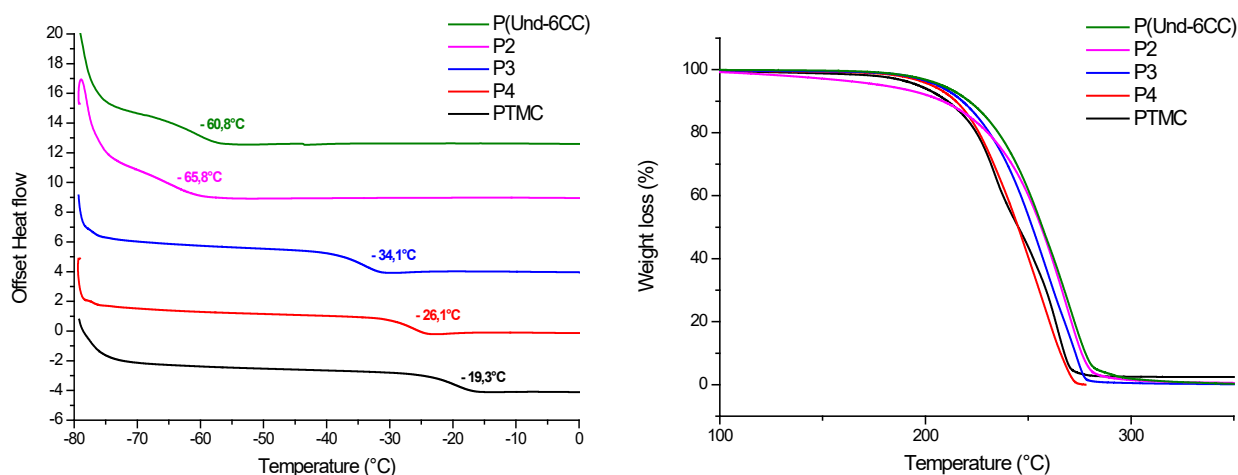


Figure 7. DSC and TGA traces of PTMC and P(Und-6CC) and of random copolymers.

The copolymers exhibit thermal stabilities ranging from 196 to 218 °C with respect to the content of bio-based carbonate functions present in the copolymer (Table 3, Figure 7). As can be seen, the incorporation of pendant alkyl chains on the polycarbonate backbone does not affect dramatically the thermal stability of the copolymers. Another series of polymerization were performed from **Ole-6CC**, **Ric-6CC** and **Lin-6CC** in toluene ($[\text{bio-based monomer}]_0 = 4 \text{ mol.L}^{-1}$), at 120°C for 48 hours using $\text{Sn}(\text{Oct})_2$ as catalyst and benzyl alcohol as initiator with $[\text{Und-6CC}]_0/[\text{Catalyst}]_0/[\text{BnOH}]_0$ ratio of 100:1:1. The objective of this study is to see the influence of the starting fatty acid on the polymer properties.

Table 3. ROP of Bio-Based Cyclic Monomers from Different Fatty Acid Derivatives^a

Polymer	Yield (%)	M_n (g.mol ⁻¹) ^b	DP	$[\mathcal{D}]^b$	T_g (°C) ^c	T_d (°C) ^d
P(Und-6CC)	13	2 500	11	1.25	-60.8	218
P(Ole-6CC)	25	5 950	18	1.34	-80.7	222
P(Lin-6CC)	18	3 100	10	1.17	-30.0	230
P(Ric-6CC)	15	2 600	8	1.35	-54.8	218

^areaction conditions: 1 mol % of BnOH, 1 mol % of $\text{Sn}(\text{Oct})_2$, 120°C, 48h; ^bEstimated by SEC with polystyrene standards; ^cMeasured from the second heating run of DSC; ^d Determined by TGA at 10°C.min⁻¹ under nitrogen after 5 wt.% loss.

At a first glance, the very low yields indicate that the long pendant alkyl chain on the cyclic carbonate tends to deactivate the monomer or the catalyst. In addition, the resulting bio-based polycarbonates exhibit rather low molar mass although the dispersity remained relatively narrow. The degree of polymerization remains between 10 and 20 which is very low compared to the targeted one (DP=100).

Regarding the polymer thermal properties, increasing the number of carbon atoms in the side chain makes the T_g of the polymer lower. Indeed, P(**Ole-6CC**) bearing 16 carbon atoms in side chain displays a T_g of -80.7°C whereas P(**Ole-6CC**) bearing only 9 carbon atoms as side chain has a T_g of -60.8°C. Therefore, the T_g of such lipidic polycarbonate could be tailored by the length of the side chain. In addition, the T_g is also influenced by the number of unsaturations present on the side chain. For a same chain length, a polycarbonate with two double bonds on the lateral chain (P(**Lin-6CC**)) exhibits a T_g fifty degrees higher than a polycarbonate having a unique unsaturation (P(**Ole-6CC**)), -80.7°C and -30.0°C respectively. This feature could be the consequence of some arrangements of the polymer chains due to the conjugated double bonds. As expected, the polymerization of **Ric-6CC** yields to a low molar mass polymer which is most probably hyper-branched due to hydroxyl functions on the monomer side chain. Concerning the thermal stability, the length and the number of unsaturations does not affect significantly the properties of the resulting polycarbonates.

To summarize, the ability of lipidic 6CCs (**Und-6CC**, **Ole-6CC**, **Lin-6CC**, **Ric-6CC**) to undergo ring-opening polymerization has been evaluated. First, different catalysts were screened in the copolymerization of **Und-6CC** with TMC (feed ratio: 10/90). The best catalyst in terms of activity, polymer molar mass and **Und-6CC**

incorporation was the tin-based compound $\text{Sn}(\text{Oct})_2$. Then, keeping the latter as catalyst, different monomer feed ratios were applied to synthesize various copolymers with different content of **Und-6CC** incorporated in the PTMC backbone. The resulting aliphatic polycarbonates exhibited tunable properties depending on **Und-6CC** content in the copolymer. As an example, a copolymer with 4.1 mol.% of **Und-6CC** displays a T_g of -26.1°C whereas the T_g decreases to -65.8°C for 34 mol.% of **Und-6CC** incorporated in the copolymer. Finally, the bio-based 6CCs have been homopolymerized using $\text{Sn}(\text{Oct})_2$ as catalyst for 48h reaction. Such bio-based polycarbonates exhibit low T_g s with low molar masses ($\text{DP} \approx 10$) due to a poor reactivity of the monomers with long pendant side chains.

Polycarbonate Crosslinking

Finally cross-linking of these polycarbonates were evaluated by several methods such as thiol-ene chemistry, epoxide-amine coupling or cross-metathesis (Figure 8). The linear precursor used in this study is $\text{P}(\text{TMC-co-Und-6CC})$ containing 9.1 mol.% of pendent double bond units (**P3**).

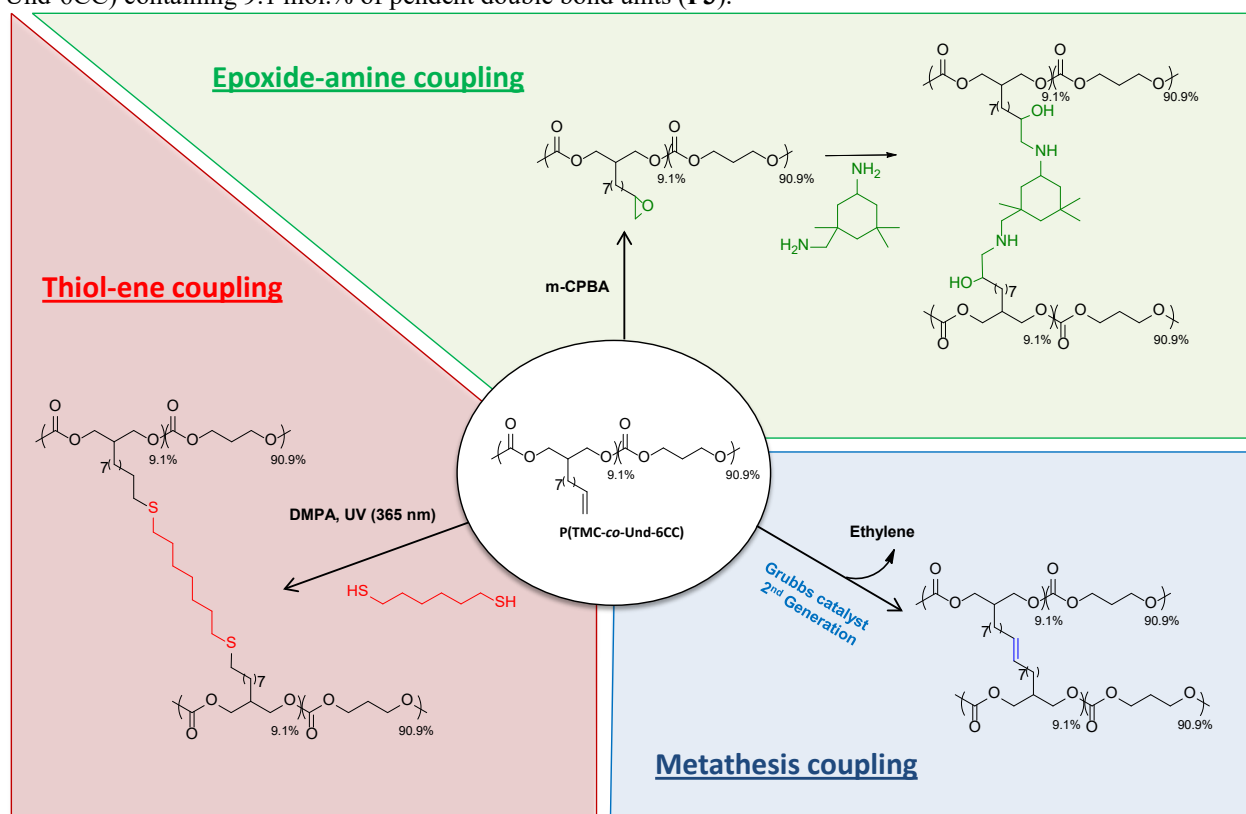


Figure 8. Cross-linking of $\text{P}(\text{TMC-co-Und-6CC})$ by three methodologies.

In the thiol-ene coupling, 1,6-hexanedithiol (HDT) was used as cross-linker with a stoichiometric amount of HDT with respect to unsaturations (i.e., 0.50 equiv. vs olefin units in the polymer) in order to reach the highest cross-linking density. The polymer, HDT and the radical initiator DMPA (1 mol.% compared to olefin units) were dissolved in DCM (2 mol.L^{-1}) and transferred to a Teflon mold. The solvent was then gently evaporated overnight and residual DCM was removed under reduced pressure during 4h. The mixture was then irradiated at 365 nm during 4 hours. An insoluble cross-linked polycarbonate was successfully obtained and characterized. As indicated in Table 4, the glass-transition temperature (T_g) and the thermal stability ($T_{d(5\%)}$) increase after the cross-linking reaction ($+7.3^\circ\text{C}$ and $+38.3^\circ\text{C}$ respectively) even though only 9.1 mol.% of functional units are present in the polymer.

Table 4. Thermal Properties Of Cross-Linked Polycarbonate from P(TMC-co-Und-6CC)

Sample	T_g^a (°C)	$T_{d(5\%)}^b$ (°C)
P(TMC-co-Und-6CC) with 9.1 mol.% of olefin units	-33.9	206.1
Network cross-linked by thiol-ene coupling	-26.6	244.4
Network cross-linked by epoxide-amine coupling	-20.9	240.3
Network cross-linked by cross-metathesis coupling	-18.9	211.1

^aDetermined by DSC at 10°C.min⁻¹ from the second cycle; ^bDetermined by TGA after 5 wt.% loss.

The second cross-linking method often used to produce epoxy thermosets involves the coupling reaction between an oxirane group and an amine.⁷² The oxirane units were obtained by epoxidizing the terminal double bond. Four equivalents of meta-chloroperoxybenzoic acid (m-CPBA) with respect to olefin units were used as oxidizing agent and the reaction was performed in refluxing chloroform during 12 hours. The structure of the epoxy-functionalized polycarbonate was followed by ¹H NMR (Figure 9) by the total disappearance of characteristic signals of olefin groups (5.0 and 5.8 ppm) and the appearance of the specific peaks attributed to epoxy ring (2.46, 2.75 and 2.90 ppm). The so-formed epoxy-functionalized polycarbonate was cross-linked in a second stage by addition of 0.50 equiv. vs oxirane groups of isophorone diamine (IPDA) in bulk. The mixture was cured at 80°C during 2 hours. The thermal properties of the cross-linked material are detailed in Table 4. As observed with thiol-ene cross-linking, both T_g and thermal stability are increased upon cross-linking by epoxy-amine coupling. Indeed, T_g increases from -33.9°C to -20.9 °C and $T_{d(5\%)}$ increases from 206.1°C to 240.3°C.

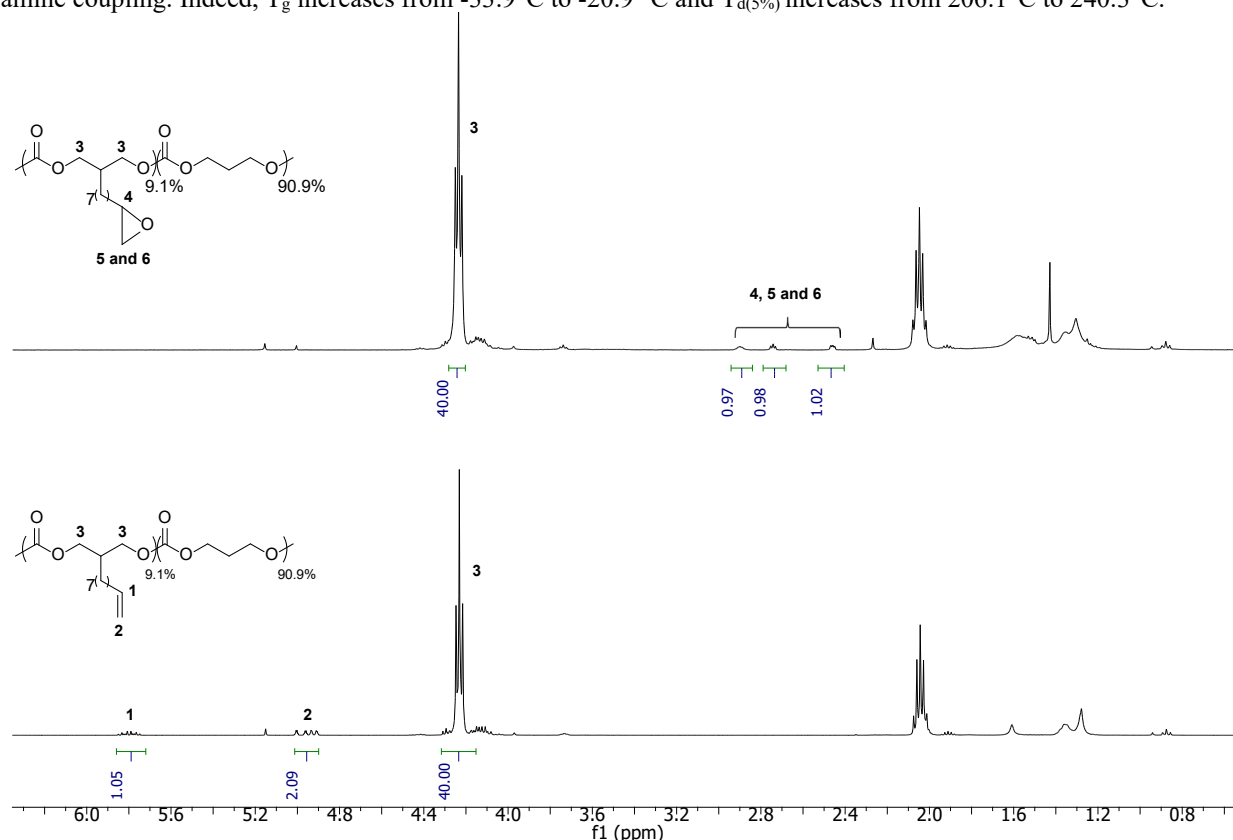


Figure 9. Stacked ¹H NMR of P(TMC-co-Und-6CC) and epoxidized P(TMC-co-Und-6CC) in CDCl₃.

The last curing method is based on the metathesis reaction. Olefin cross-metathesis and ring-closing metathesis are widely used in polymer chemistry.^{73,74} For example, olefin cross-metathesis has been used to cross-link and stabilize supramolecular assemblies, including cylindrical peptide assemblies,⁷⁵ the shells of polymeric micelles⁷⁶ and the peripheries of dendrimers.⁷⁷ Metathesis reactions of linear polymer chains with pendent vinyl groups give a range of results, depending on reaction conditions. When the vinyl groups are located at suitable distances for cyclization, formation of rings along the chain occurs.⁷⁸ When the vinyl groups are spaced too far

apart for convenient ring-closing metathesis, functional groups can be attached through olefin cross-metathesis.⁷⁹ In the absence of a cross-metathesis partner, the polymer undergoes cross-linking, which can be limited to intramolecular cross-linking under dilute conditions.⁸⁰

In this study, the preparation of a cross-linked polycarbonate was attempted by olefin cross-metathesis thanks to pendent olefin groups. Grubbs catalyst 2nd generation has been used with a loading of 2 mol.% with respect to olefin units. As above-mentioned, only intramolecular cross-linking occur under dilute conditions. Therefore, the cross-linking was performed in DCM at high concentration (4 mol.L⁻¹) to favor intermolecular process. After 12h of reaction at room temperature, a cross-linked polycarbonate was successfully synthesized. The thermal properties of the obtained network are shown in Table 4. Even though the thermal stability of the network remains similar compared to the polymer, the network T_g increases from -33.9°C to -18.9°C.

Conclusion

In conclusion, several methods were utilized affording successfully polycarbonate network structures. In terms of thermal properties, all the obtained networks exhibit similar T_g and thermal stability. However, the direct cross-linking (no need of post-polymerization reaction) in thiol-ene and metathesis couplings is an advantage in comparison to the epoxide-amine reaction. In addition, the easiness of the process and the capacity to control the cross-linking density through the thiol-ene reaction make this coupling methodology more versatile with respect to the cross-metathesis coupling.

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References

- (1) Rokicki, G.; Parzuchowski, P. G. G. *ROP of cyclic carbonates and ROP of macrocycles*; Elsevier, 2012; Vol. 4.
- (2) Montero De Espinosa, L.; Meier, M. A. R.; De Espinosa, L.; Meier, M. A. R. *Eur. Polym. J.* **2011**, *47* (5), 837–852.
- (3) Maisonneuve, L.; Wirotius, A.-L.; Alfos, C.; Grau, E.; Cramail, H. *Polym. Chem.* **2014**, *5* (21), 6142–6147.
- (4) Lamarzelle, O.; Durand, P.-L.; Wirotius, A.-L.; Chollet, G.; Grau, E.; Cramail, H. *Polym. Chem.* **2016**, *7*, 1439–1451.
- (5) Durand, P.L.; Brège, A.; Chollet, G.; Grau, E.; Cramail H. *ACS Macro Letters*, **2018**, *7* (2), 250-254
- (6) Durand, P.L.; Chollet, G.; Grau, E.; Cramail H. *RSC Advances*, **2019**, *9* (1), 145-150
- (7) Durand, P.L.; Grau, E.; Cramail H. *Molecules*, **2020**, *25* (1), 74
- (8) Kolb, N.; Meier, M. A. R. *Eur. Polym. J.* **2012**, *49* (4), 843–852.
- (9) Kolb, N.; Meier, M. A. R.; Wadgaonkar, P. P.; Swett, L. R.; Wang, T. S.; Sommers, A. H.; DeNet, R. W. *Green Chem.* **2012**, *14* (9), 2429.
- (10) Rokicki, G. *Prog. Polym. Sci.* **2000**, *25* (2), 259–342.
- (11) Hu, B.; Zhuo, R.; Fan, C. *Polym. Adv. Technol.* **1998**, *9* (2), 145–149.
- (12) Albertson, A. C.; Ann, C.; Sjoling, M. *J. Macromol. Sci. Pure Appl. Chem.* **1992**, *29* (1), 43–54.
- (13) Clements, J. H. *Ind. Eng. Chem. Res.* **2003**, *42* (4), 663–674.
- (14) Pyo, S.-H.; Persson, P.; Lundmark, S.; Hatti-Kaul, R. *Green Chem.* **2011**, *13* (4), 976–982.
- (15) Pyo, S.-H.; Hatti-Kaul, R. *Adv. Synth. Catal.* **2012**, *354* (5), 797–802.
- (16) Nohra, B.; Candy, L.; Blanco, J.-F.; Raoul, Y.; Mouloungui, Z. *Eur. J. Lipid Sci. Technol.* **2012**, *115* (1), 111–122.
- (17) Luo, X.; Huang, F.; Qin, S.; Wang, H.; Feng, J.; Zhang, X.; Zhuo, R. *Biomaterials* **2011**, *32* (36), 9925–9939.
- (18) Parzuchowski, P. G.; Jaroch, M.; Tryznowski, M.; Rokicki, G. *Macromolecules* **2008**, *41* (11), 3859–3865.

- (19) Su, W.; Luo, X.; Wang, H.; Li, L.; Feng, J.; Zhang, X.-Z.; Zhuo, R. *Macromol. Rapid Commun.* **2011**, *32* (4), 390–396.
- (20) Wang, X. L.; Zhuo, R. X.; Huang, S. W.; Liu, L. J.; He, F. *Macromol. Chem. Phys.* **2002**, *203* (7), 985–990.
- (21) Ray, W.; Grinstaff, M. *Macromolecules* **2003**, *1*, 3557–3562.
- (22) Mei, H.; Zhong, Z.; Long, F.; Zhuo, R. *Macromol. Rapid Commun.* **2006**, *27* (22), 1894–1899.
- (23) Wu, R.; Al-Azemi, T. F.; Bisht, K. S. *Biomacromolecules* **2008**, *9* (10), 2921–2928.
- (24) Vandenberg, E. J.; Tian, D. *Macromolecules* **1999**, *32* (11), 3613–3619.
- (25) Xu, J.; Liu, Z. L.; Zhuo, R. X. *J. Appl. Polym. Sci.* **2006**, *101* (3), 1988–1994.
- (26) Xie, Z.; Lu, C.; Shi, Q.; Jing, X. *J. Polym. Sci. Part A Polym. Chem.* **2007**, *45*, 1737–1745.
- (27) Lie, M. S. F.; Jie, K. *Eur. J. Lipid Sci. Technol.* **2001**, *103*, 594–632.
- (28) Marcel, S. F.; Pasha, M. K.; Alam, M. S.; Jie, L. K. *Lipids* **1997**, *32* (10), 1041–1044.
- (29) Gunstone, F. D.; SAID, A. *Chem. Phys. Lipids* **1971**, *7*, 121–134.
- (30) Sanda, F.; Kamatani, J.; Endo, T. *Macromolecules* **2001**, *34* (6), 1564–1569.
- (31) Chen, W.; Meng, F.; Li, F.; Ji, S.-J.; Zhong, Z. *Biomacromolecules* **2009**, *10* (7), 1727–1735.
- (32) Kühling, S.; Keul, H.; Höcker, H. *Die Makromol. Chemie* **1992**, *193* (5), 1207–1217.
- (33) Weilandt, K. D.; Keul, H.; Höcker, H. *Macromol. Chem. Phys.* **1996**, *197* (11), 3851–3868.
- (34) Chen, W.; Yang, H.; Wang, R.; Cheng, R.; Meng, F.; Wei, W.; Zhong, Z. *Macromolecules* **2010**, *43* (1), 201–207.
- (35) He, F.; Wang, Y.-P. P.; Liu, G.; Jia, H.-L. L.; Feng, J.; Zhuo, R.-X. X. *Polymer (Guildf)*. **2008**, *49* (5), 1185–1190.
- (36) Zhang, X.; Mei, H.; Hu, C.; Zhong, Z.; Zhuo, R. *Macromolecules* **2009**, *42* (4), 1010–1016.
- (37) Chen, X.; Mccarthy, S. P.; Gross, R. a. *Macromolecules* **1997**, *30*, 3470–3476.
- (38) Shen, Y.; Chen, X.; Gross, R. A. *Macromolecules* **1999**, *32* (12), 3891–3897.
- (39) Al-Azemi, T. F.; Bisht, K. S. *Macromolecules* **1999**, *32* (20), 6536–6540.
- (40) Sanders, D. P.; Fukushima, K.; Coady, D. J.; Nelson, A.; Fujiwara, M.; Yasumoto, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2010**, *132* (42), 14724–14726.
- (41) Pratt, R. C.; Nederberg, F.; Waymouth, R. M.; Hedrick, J. L.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2008**, 114–116.
- (42) Tempelaar, S.; Mespouille, L.; Coulembier, O.; Dubois, P.; Dove, A. P. *Chem. Soc. Rev.* **2013**, *42* (3), 1312–1336.
- (43) Mindemark, J.; Bowden, T. *Polymer (Guildf)*. **2011**, *52* (25), 5716–5722.
- (44) Al-Azemi, T. F.; Bisht, K. S. *Polymer (Guildf)*. **2002**, *43* (8), 2161–2167.
- (45) Hou, Q.; Grijpma, D. W.; Feijen, J. *Acta Biomater.* **2009**, *5* (5), 1543–1551.
- (46) Kricheldorf, H. R.; Stricker, A. *Macromol. Chem. Phys* **2000**, *201* (17), 2557–2565.
- (47) Chen, F.; Amsden, B. G. *J. Polym. Sci. Part A Polym. Chem.* **2015**, 1–9.
- (48) Mindemark, J.; Törmä, E.; Sun, B.; Brandell, D. *Polymer (Guildf)*. **2015**, *63*, 91–98.
- (49) Edlund, U.; Albertsson, A. *J. Appl. Polym. Sci.* **1999**, *72*, 227–239.
- (50) Wang, H.; Dong, J. H. U. A.; Qiu, K. U. N. Y.; Gu, Z. W. E. I. *J. Polym. Sci. Part A Polym. Chem.* **1998**, *36*, 1301–1307.
- (51) Trimaille, T.; Moller, M.; Gurny, R. *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42* (17), 4379–4391.
- (52) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* **2010**, *43* (5), 2093–2107.
- (53) Dove, A. P. *Chem. Commun.* **2008**, 6446–6470.
- (54) Helou, M.; Miserque, O.; Brusson, J.-M. M.; Carpentier, J.-F. F.; Guillaume, S. M. *Chem. - A Eur. J.* **2010**, *16* (46), 13805–13813.
- (55) Kazakov, O. I.; Datta, P.; Isajani, M.; Kiesewetter, E. T.; Kiesewetter, M. K. *Macromolecules* **2014**, *47*, 7463–7468.
- (56) Nederberg, F.; Lohmeijer, B. G. G.; Leibfarth, F.; Pratt, R. C.; Choi, J.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *Biomacromolecules* **2007**, *8* (1), 153–160.
- (57) Tempelaar, S.; Mespouille, L.; Dubois, P.; Dove, A. P. *Macromolecules* **2011**, *44* (7), 2084–2091.
- (58) Venkataraman, S.; Ng, V. W. L.; Coady, D. J.; Horn, H. W.; Jones, G. O.; Fung, T. S.; Sardón, H.; Waymouth, R. M.; Hedrick, J. L.; Yang, Y. Y. *J. Am. Chem. Soc.* **2015**, *137* (43), 13851–13860.
- (59) Cho, S.; Heo, G. S.; Khan, S.; Gonzalez, A. M.; Elsabahy, M.; Wooley, K. L. *Macromolecules* **2015**, *48* (24), 8797–8805.
- (60) Pati, D.; Feng, X.; Hadjichristidis, N.; Gnanou, Y. *Macromolecules* **2017**, *50* (4), 1362–1370.
- (61) Kuroishi, P. K.; Bennison, M. J.; Dove, A. P. *Polym. Chem.* **2016**, *7* (46), 7108–7115.
- (62) Olsson, J. V.; Hult, D.; Cai, Y.; Garcia-Gallego, S.; Malkoch, M. *Polym. Chem.* **2014**, *5* (23), 6651–6655.
- (63) Williams, R. J.; Barker, I. A.; O'Reilly, R. K.; Dove, A. P. *ACS Macro Lett.* **2012**, 1285–1290.

- (64) Tezuka, K.; Koda, K.; Katagiri, H.; Haba, O. *Polym. Bull.* **2015**.
- (65) Ganivada, M. N.; Kumar, P.; Kanjilal, P.; Dinda, H.; Sarma, J. Das; Shunmugam, R. *Polym. Chem.* **2016**, *7*, 4237.
- (66) Onbulak, S.; Tempelaar, S.; Pounder, R. J.; Gok, O.; Sanyal, R.; Dove, A. P.; Sanyal, A. *Macromolecules* **2012**, *45* (3), 1715–1722.
- (67) Pascual, A.; Tan, J. P. K.; Yuen, A.; Chan, J. M. W.; Coady, D. J.; Mecerreyes, D.; Hedrick, J. L.; Yang, Y. Y.; Sardon, H. *Biomacromolecules* **2015**, *16* (4), 1169–1178.
- (68) Xie, M.; Yu, L.; Li, Z.; Zheng, Z.; Wang, X. *J. Polym. Sci. Part A Polym. Chem.* **2016**, *54* (22), 3583–3592.
- (69) De la rosa, V. R.; Tempelaar, S.; Dubois, P.; Hoogenboom, R.; Mespouille, L. *Polym. Chem.* **2016**, *7*, 1559–1568.
- (70) Voo, Z. X.; Khan, M.; Narayanan, K.; Seah, D.; Hedrick, J. L.; Yang, Y. Y. *Macromolecules* **2015**, *48*, 1055–1064.
- (71) Thomas, A.; Kuroishi, P.; Perez-Madriral, M.; Whittaker, A.; Dove, A. P. *Polym. Chem.* **2017**.
- (72) Vidil, T.; Tournilhac, F.; Musso, S.; Robisson, A.; Leibler, L. *Prog. Polym. Sci.* **2016**, *62*, 126–179.
- (73) Sinclair, F.; Alkattan, M.; Prunet, J.; Shaver, M. P. *Polym. Chem.* **2017**, *8* (22), 3385–3398.
- (74) Neal, J. A.; Mozhdehi, D.; Guan, Z. *J. Am. Chem. Soc.* **2015**, *137* (14), 4846–4850.
- (75) Clark, T. D.; Kobayashi, K.; Ghadiri, M. R. *Chem. - A Eur. J.* **1999**, *5* (2), 782–792.
- (76) Skaff, H.; Lin, Y.; Tangirala, R.; Breitenkamp, K.; Böker, A.; Russell, T. P.; Emrick, T. *Adv. Mater.* **2005**, *17* (17), 2082–2086.
- (77) Lemcoff, N. G.; Spurlin, T. A.; Gewirth, A. A.; Zimmerman, S. C.; Beil, J. B.; Elmer, S. L.; Vandever, H. G. *J. Am. Chem. Soc.* **2004**, *126* (37), 11420–11421.
- (78) Coates, G. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118* (1), 229–230.
- (79) Mathers, R. T.; Coates, G. W. *Chem. Commun.* **2004**, 422–423.
- (80) Cherian, A. E.; Sun, F. C.; Sheiko, S. S.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129* (37), 11350–11351