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Solvent free Glycidyl Carbamates oligomerisation and solvent affinity of oligomers

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This paper is dedicated to the memory of Dr. Jean-François Tranchant who has inspired this work, and many others.

KEYWORDS: glycerol carbonate, glycidyl carbamate, oligoglycerol,

Abstract

Polyglycerols are a class of multifunctional polymers obtained from the polymerization of glycidol and its derivatives. Unlike poly(ethylene glycol) (PEG), which is the most common polyether, polyglycerols can exhibit many functionalities on their side chains and can be obtained from renewable resources, mainly glycerol. Hereby, this study will focus on glycidyl carbamates, a new class of monomers readily available from glycerol carbonate, which combines the chemical functionalities of both glycidol and urethane. The polymerization of these glycidyl ethers directly leads to linear poly(glycidyl carbamates), thus avoiding several protection and deprotection steps of the monomers or polymers. This study hence gives a first approach to glycidyl carbamate polymerization. Commonly used initiators in anionic ring-opening polymerization (alkali metal alkoxides) lead to ill-defined compounds after full conversion of the monomers, whereas pyridine derivative initiators lead to oligomers whose structures could be thoroughly described. The results suggest that low basicity and high nucleophilicity are the most suitable conditions to polymerize glycidyl carbamates because of the sensitivity of the urethane moiety. Additionally, a study of the obtained poly(glycidyl carbamates) affinity toward the solvent has been conducted to further describe the properties of these novel original polyethers.

Introduction

Polyethers constitute a class of polymers with many applications such as in the paper industry, cosmetics, or biomedical applications. They can be obtained for instance by polymerization of epoxides, such as ethylene oxide, to produce poly(ethylene glycols) (PEGs), well-known in pharmaceutical and biomedical applications for their low toxicity and good solubility. However, concerns have been raised recently due to the potential toxicity of PEGs, in particular with low-molecular-weight PEGs (up to $400 \text{ g}\cdot\text{mol}^{-1}$), or the suspected hypersensitivity induced by their usage.¹ Furthermore, the absence of functional groups within the chain limits their versatility. To access highly functionalized PEG-like polymers, functional polyethers and polyglycerols (or polyglycidols) have gained a lot of attention thanks to the presence of multiple hydroxyl groups along the chain. Glycidol, which is an epoxide-based monomer derived from glycerol, gives access to many hyperbranched and dendrimeric polyglycerols.^{2,3} To build well-defined structures of polyglycerol, synthesis of linear polyglycerol was first investigated.¹ Frey et al. have extensively reviewed the synthesis, modifications, and applications of linear polyglycerols. The main synthetic strategy requires the use of protected glycidol, such as ethoxyethyl glycidyl ether (EEGE),⁴ or commercially available allyl glycidyl ether (AGE) and tert-butyl glycidyl ether (tBuGE) for both homo- and copolymerization.⁵ Polymerization of such linear functionalized epoxides has been reviewed several times^{6,7}. The deprotection of obtained polymers under acidic conditions releases free hydroxyl moieties that can further react to form functionalized polyglycerols, with pendent ester, urethane, or carbonate groups. Such modified linear polyglycerol structures have been found in the literature through pathways involving polymerization of EEGE, its acetal deprotection, and postfunctionalization of the side chain using phenyl chloroformate and methyltriethylene-glycol amine⁸ or isocyanate.⁹ Also, in the light of interest for isocyanate-free polyurethanes combined with polyethers, main strategies have been mainly focused on the polymer side chains' functionalization where the choice of monomers is dictated by

postpolymerization possibilities rather than their potential properties once polymerized. For example, Brocas et al. described the synthesis of the polyurethane network through epichlorohydrin or allyl glycidyl ether polymerization to obtain polyethers further modified to obtain polyurethane networks in the presence of diamine.¹⁰ To our knowledge, there is at the moment no investigation on the direct synthesis of well-defined structures of linear poly(glycidyl carbamates) from glycidyl carbamate (GC) monomers. Hence, the presence of a carbamate moiety on a functional glycidol derivative opens new perspectives in terms of the synthetic pathway and of properties of the resulting polymers (thermoreversible, amphiphilic, or resinlike behaviors^{9,11,12}). The synthesis of such monomers has previously been described by our group and presents several advantages: they are prepared from glycerol, one of the most important renewable feedstock nowadays,¹³ and the urethane moieties are obtained using amines; thus, they could be seen as an alternative to the use of isocyanates and glycidol for their synthesis as well as functionalizing oligo- and polyglycerol.

Polymerization of glycidol-based monomers by anionic ring-opening polymerization is known in the literature using alkali metals as initiators, such as potassium alkoxides,^{14,15} or through activated epoxide polymerization by the ZnEt₂/H₂O catalyst,⁴ or a combination of triisobutylaluminum/alkali metalalkoxides or ammonium salt.^{16,17} Regarding metal-free polymerization of epoxides, many examples of organic initiators can be found in the literature, such as N-heterocyclic carbenes,¹⁸ phosphazene bases,¹⁹ or pyridine derivatives.²⁰

In this work, we focused our interest on the homopolymerization of glycidyl carbamates **1** (Scheme 1) using different bases as nucleophilic initiators. Glycidyl carbamates have been synthesized by a four-step synthetic pathway from glycerol carbonate, leading to one single regioisomer, where the urethane moiety is located at the β -position from the oxirane ring (NMR ¹H of the three monomers used in this article are provided in the Supporting Information). Using a metal-free initiating system, the potential of glycidyl

carbamate as a new glycerol-based monomer for the preparation of original functionalized polyglycerols will be discussed. Furthermore, the affinity of these oligomers toward solvents will be explored through an experimental approach using poly(glycidyl carbamates) in the form of thin films.

Experimental

Materials.

4-Dimethylaminopyridine (DMAP) (Acros Organics, 99%), 4-pyrrolidinopyridine (PPY) (Acros Organics, 98%), 9-azajulolidine (AJ) (Aldrich, 97%), calcium hydride (CaH_2) (Acros Organics, 93%, 10–100 mm and Alfa Aesar, 92%, coarse powder), sodium iodide (NaI) (Acros Organics, 99%), and dithranol (Sigma, 97%) were used as received. Synthesis of glycidyl N,N-carbamates was achieved using previously reported protocols from our group.²¹

Glycidyl carbamates are purified by flash chromatography. Prior to use, they are dried for 2 h over CaH_2 under a vacuum and then distilled twice under CaH_2 using a Büchi Glass Oven Kugelrohr.

Instrumentation.

^1H and ^{13}C NMR spectra were recorded in CDCl_3 using a 250 MHz Bruker Avance DPX-250 instrument or a 400 MHz Bruker Avance II 400 instrument.

Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) spectra were acquired on a Bruker Autoflex mass spectrometer.

Sample preparation and conditions for MALDI-TOF mass spectrometry (MS).

To prepare the samples, polymers, NaI, and dithranol were dissolved in tetrahydrofuran (THF) at a concentration of $10 \text{ mg} \cdot \text{mL}^{-1}$. Then, 20 μL of the dithranol solution was mixed with 5 μL of the polymer sample and 5 μL of NaI into a 0.5 mL Eppendorf tube; then, 0.5 μL of the solution was spotted on a stainless steel MALDI plate. The solvent was evaporated at room temperature before insertion of the plate into the source.

Each sample was analyzed in linear and reflectron positive ionization modes using the following instrumental settings on FlexControl (v. 3.4).

Reflectron method: ion source 1 at 19 kV, ion source 2 at 16.7 kV, lens 8.4 kV, reflector 21.11 kV, and pulsed ion extracted at 150 ns for the positive mode with a laser frequency of 100 Hz ($\lambda = 355 \text{ nm}$).

Linear method: ion source 1 at 19.5 kV, ion source 2 at 18.3 kV, lens 7 kV, and pulsed ion extracted at 400 ns for the positive mode with a laser frequency of 100 Hz. Laser power was adapted to obtain significant signal-to-noise (S/N) ratio and a good resolution of the mass peaks.

Mass spectra were recorded in the range 400–5000 Da in the reflectron mode and 1–15 kDa in the linear mode. To improve the S/N ratio, each measured spectrum represented the summations of four times five hundred laser shots. Mass calibration between 400 and 10 000 Da was performed externally with poly(ethylene oxide) (PEO, $M_n = 1000, 2000, 4000, \text{ and } 5000 \text{ g} \cdot \text{mol}^{-1}$) following the same procedure as described for the polymers (except that PEO was dissolved in a mixture of 50:50 water/acetonitrile). The calibrant ions were detected under a sodium adduct form. The calibration was done with a cubic enhanced algorithm and last fit error of about 30 ppm.

MALDI peak picking, average masses (M_n), and degree of polymerization (DP) of the polymers were determined using FlexAnalysis (v. 3.4) and PolyTools (v. 1.3.1) software (Bruker).

Thin-Film Preparation and Swelling Measurements.

Thin films were obtained by depositing a $30 \text{ mg}\cdot\text{mL}^{-1}$ solution of the studied polymer in dichloromethane on silicon substrates ($1 \times 1 \text{ cm}^2$) by spin-coating at 3600 rpm for 30 s. For swelling measurement, the thickness of the films was continuously measured by visible reflectometry (F20, Filmetrics) during an exposure to solvent vapors in a closed poly(tetrafluoroethylene) (PTFE) chamber (total volume of 20 mL) equipped with a transparent lid (allowing for thickness measurement) and containing 1.5 mL of the liquid solvent at the bottom (dichloromethane, ethyl acetate, THF, toluene, cyclohexane, water, acetone, methanol, isopropanol, and ethanol). A partial solvent vapor pressure of 0.8 was maintained in the chamber by mixing the liquid solvent ($80\% \text{ mol}\cdot\text{mol}^{-1}$) with a nonvolatile solute ($20\% \text{ mol}\cdot\text{mol}^{-1}$). The following nonvolatile solutes were used: squalene for dichloromethane, ethyl acetate, THF, toluene, and cyclohexane; glycerol for water, acetone, methanol, isopropanol, and ethanol.

Polymerization of Glycidyl N,N-Carbamates.

This general procedure applies to each of the three different glycidyl carbamates (GCs). The polymerizations of glycidyl carbamate were carried out in screw-cap sealed tubes under an argon atmosphere. Tubes were previously dried in an oven at $110 \text{ }^\circ\text{C}$ overnight and cooled down in a dry atmosphere. Then, freshly distilled glycidyl carbamate was added under an argon atmosphere (500 mg) through a septum and left under a vacuum for one more hour. Then, the desired amount of initiator was added to the tube and sealed under argon with a screw- cap. The reaction mixture was stirred at $50 \text{ }^\circ\text{C}$ for the required amount of time. ^1H NMR was performed after 24–96 h to monitor the conversion of the GC. The reaction was stopped by addition of 2 mL of ethanol and evaporated under reduced pressure at room temperature, giving a dark-brown sticky paste.²⁰

Poly(glycidyl N,N-dimethylcarbamate): 1b. ^1H NMR (CDCl_3 , 250 MHz): 8.2 (d, DMAP-aromatic), 6.4 (d, DMAP-aromatic), 5.1–4.7 (m, $-\text{CH}-\text{OCON}-$), 3.4–4.3 (m, $-\text{CH}_2\text{CHO}-$ polymer backbone, $\text{CH}-\text{CH}_2\text{O}-$ polymer side chain), 3.2 (s, DMAP- $(\text{CH}_3)_2$), 2.9 (s, $-\text{N}-(\text{CH}_3)_2$).

^{13}C NMR (CDCl_3 , 100 MHz): 156.2 (C-carbamate), 72.4 ($\text{CH}-\text{O}$ -carbamate), 68.8–72.0 ($-\text{O}-\text{CH}_2-\text{CH}-\text{O}-$ polymer backbone), 64.4 ($-\text{CH}_2-\text{O}$ -carbamate, polymer side chain), 35.8–35.3 ($-\text{N}-(\text{CH}_3)_2$).

Poly(glycidyl N-piperidinylcarbamate): 2a. ^1H NMR (CDCl_3 , 250 MHz): 8.2 (d, DMAP-aromatic), 6.4 (d, DMAP-aromatic), 5.1–4.7 (m, $-\text{CH}-\text{OCON}-$), 3.4–4.3 (m, $-\text{CH}_2\text{CHO}-$ polymer backbone, $-\text{CH}-\text{CH}_2\text{O}-$ polymer side chain), 3.3 (br, $(\text{CH}_2)_2\text{-N}$ -carbamate), 3.0 (s, DMAP- $(\text{CH}_3)_2$), 1.5 (br, $(\text{CH}_2)_3$ -piperidinyl).

^{13}C NMR (CDCl_3 , 100 MHz): 156.2 (C-carbamate), 72.4 ($\text{CH}-\text{O}$ -carbamate), 68.8–72.0 ($-\text{O}-\text{CH}_2-\text{CH}-\text{O}-$ polymer backbone), 64.4 ($-\text{CH}_2-\text{O}$ -carbamate, polymer side chain), 35.8–35.3 ($-\text{N}-64.0$ ($-\text{CH}_2-\text{O}$ -carbamate, polymer side chain), 44.4 ($(\text{CH}_2)_2\text{-N}$ -carbamate), 23.9, 25.3 ($(\text{CH}_2)_3$ -piperidinyl).

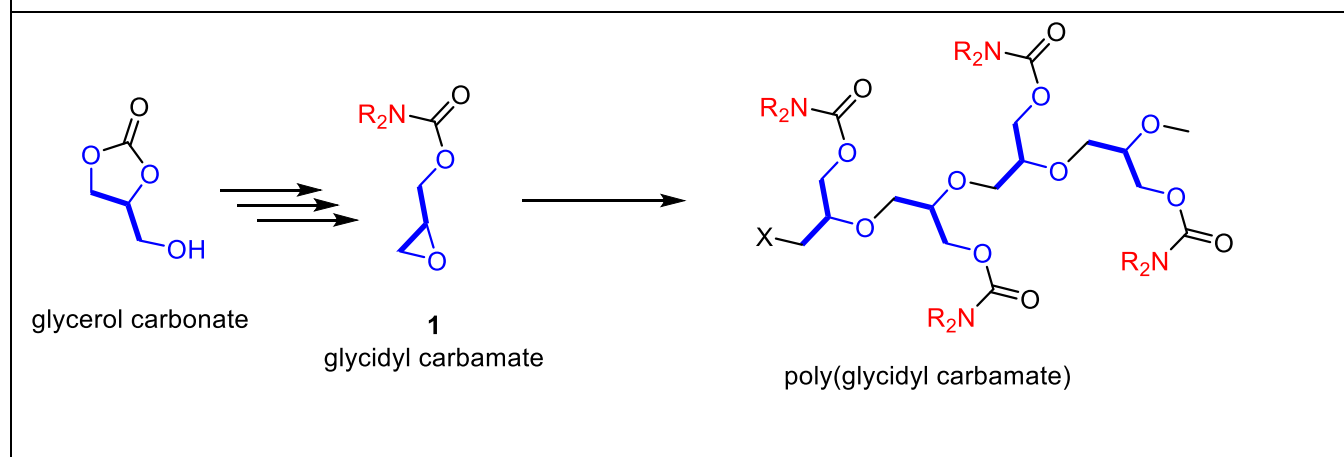
Poly(glycidyl N-morpholinylcarbamate): 3a. ^1H NMR (CDCl_3 , 250 MHz): 8.2 (d, DMAP-aromatic), 6.4 (d, DMAP-aromatic), 5.1–4.7 (m, $-\text{CH}-\text{OCON}-$), 3.9–4.2 (br, $-\text{CH}-\text{CH}_2\text{O}-$ polymer side chain), 3.3–3.7 (br $-\text{CH}_2\text{CHO}-$ polymer backbone; $(\text{CH}_2)_2\text{-N}$ -carbamate; $(\text{CH}_2)_2\text{-O}$ -carbamate), 3.0 (s, DMAP- $(\text{CH}_3)_2$)

^{13}C NMR (CDCl_3 , 100 MHz): 155.1 (C-carbamate), 72.7 (CH -carbamate), 68.8–71.9 ($-\text{O}-\text{CH}_2-\text{CH}-\text{O}-$ polymer backbone), 66.5 ($-\text{O}-\text{O}-\text{O}-\text{O}-$ carbamate), 64.5 ($-\text{CH}_2-\text{O}$ -carbamate, polymer side chain), 44.2 ($(\text{CH}_2)_2\text{-N}$).

Derivatization of Poly(glycidyl N,N-dimethylcarbamate).

First, 100 mg of poly(glycidyl N,N-dimethylcarbamate) 1b was dissolved in CH₂Cl₂ at 0.3 M and stirred with a magnetic stirrer. Then, 0.5 equiv of 3-phenylpropionyl chloride regarding the theoretical molar quantity of 1b was added to the mixture and heated at reflux for 1 h. The reaction was then evaporated under reduced pressure.

Scheme 1 : General Strategy Toward Poly(glycidyl carbamates) from Glycidyl Carbamates 1

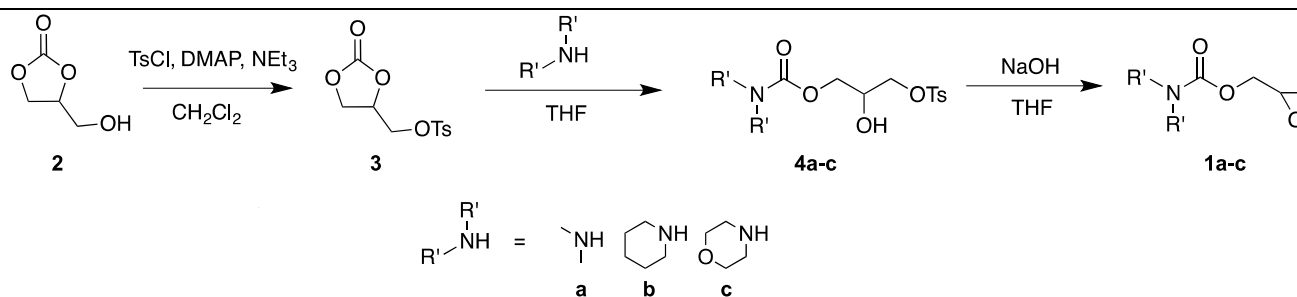


Results and discussion

From previous results within the group, the synthesis of N,N- glycidyl carbamates 1 (Scheme 2) is a three-step process starting from glycerol carbonate 2, a renewable molecule.^{21–23} It involves the activation of the primary alcohol as a sulfonate using tosyl chloride to form the tosylated glycerol carbonate 3. This cyclic carbonate then reacts with a primary or a secondary amine, leading to the formation of the carbamate function. We have shown that just a short range of disubstituted amines could be used for this opening: only cyclic secondary amines and dimethylamine proved to be sufficiently reactive to regioselectively ring-open the carbonate and form carbamate 4. The last step is the intramolecular nucleophilic substitution of the O-tosyl group by the secondary alcohol under basic conditions to form epoxide 1. We focused our

study on three monomers derived from dimethylamine **a**, piperidine **b**, and morpholine **c**. These reactions were optimized on a multigramscale and obtained with good global yields ranging from 58 to 74% over three steps.

Scheme 2: Synthesis of N,N-glycidyl carbamates **1a-c** from glycerol carbonate **2**



Preliminary Polymerization Tests.

Table 1. Polymerization of Glycidyl N,N-Dimethylcarbamate (GDMC, 1a) Using Strong Bases as Initiators^{a,b}

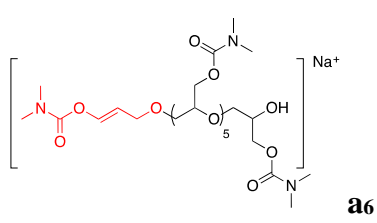
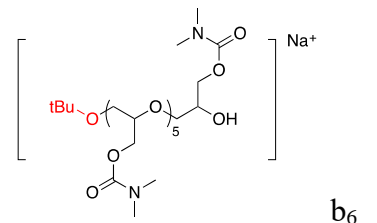
Entry	Initiator	[I]/[M]	Time (h)	conv. ^a (%)	\overline{M}_n (theo.) (g.mol ⁻¹)	\overline{DP} (theo.)	\overline{M}_n MALDI-ToF ^b (g.mol ⁻¹)	\overline{DP} MALDI-ToF ^b
1	t-buOK	0.05	72	>99	2900	20	1300	9
2		0.05	24	97	2900	20	1580	11
3	t-buONa	0.025	168	>99 ^c	5800	40	- ^c	-
4		0.075	168	>99 ^c	1890	13	- ^c	-
5		0.125	168	>99	1190	8	1670	13
6	PPOH P ₄ -tBu	0.02 0.025	264	>99	7250	50	- ^c	-

All reactions were performed at 50°C in THF except entry 2 which was performed without solvent. [I]/[M] correspond to initiator/monomer molar ratios^a Determined by ¹H NMR spectroscopy: >99% indicates the total disappearance of epoxide characteristic signals; ^b Determined by MALDI-ToF, using the software Polytools; ^c Determined by ¹H NMR spectroscopy, complete disappearance of monomer, no detection of polymers using MALDI-ToF.

In a metal-free approach of functionalized epoxide polymerization, we first explored various bases including potassium-tert-butoxide (t-BuOK), sodium tert-butoxide (t-BuONa), phosphazene bases, and pyridine derivatives as initiators on the model monomer glycidyl N,N-dimethylcarbamate (GDMC, 1a). Table 1 : Polymerization of N,N-dimethylglycidylcarbamate (GDMC, 1a) using strong bases as initiators. Our first tests using classical strong bases t-BuOK, t-BuONa, and phosphazene showed poor reliability. t-BuOK ([I]/[M] = 0.05) was used in THF as the solvent or under neat conditions (**Table 1**). The conversion, followed by ¹H NMR spectroscopy looking at the disappearance of characteristic epoxide

signals, was complete in 72 and 24 h, respectively, for entries 1 and 2, and the poly(glycidyl carbamate) oligomer characterization (molecular weight averages (M_n) and (M_w), degree of polymerization (DP), polydispersity, mass of repeat unit, and end-group mass structure) could be performed thanks to matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) in linear and reflectron modes, using the dithranol matrix (for the best ionization process in our case). Despite a good conversion, the presence of several distributions in each sample could be noticed by MALDI-TOF MS in the linear mode with a lower DP value in THF than using the neat conditions (of 9 and 11, respectively). Furthermore, the resulting M_n was lower than the theoretical ones. In the case of polymers with high polydispersity ($\mathcal{D} > 1.2$), most studies indicate that MALDI data underestimate the high-mass components, resulting in significantly lower average molecular weight values. One of the reasons for this bias for polymers (in particular with a $\mathcal{D} > 1.2$) seems to be mainly related to the sampling and acquisition conditions of MALDI.^{24,25} Being aware of this constraint, we have tried to minimize these effects by selecting the most favorable matrix preparation (dithranol), matrix/analyte ratio, and desorption conditions (described before) for the characterization of our calibrant and samples with a satisfactory degree of confidence. In this case, MALDI results provide a preliminary characterization of the oligomer structures sufficient to consider modulations in the synthetic conditions. We then changed the counterion from potassium to sodium and tested t-BuONa. In this case, the complete conversion was observed at $[I]/[M] = 0.025$ and 0.075 , but the MALDI analysis showed only few signals of ionization and low DPs were obtained even after 168 h of reaction (entries 3 and 4). The oligomerization was finally detected using t-BuONa at the ratio $[I]/[M] = 0.125$ (entry 5). Quite unexpectedly, the observed DP (13) was higher than the theoretical one (8), which could be attributed to an unfavorable kinetic effect on the initiation step in comparison with the propagation one. We also have tested a phosphazene reagent alone (t-BuP₄) (**Table 1**, entry 6) as an organic initiator, which turned out to be too reactive: full conversion (i.e., transformation)

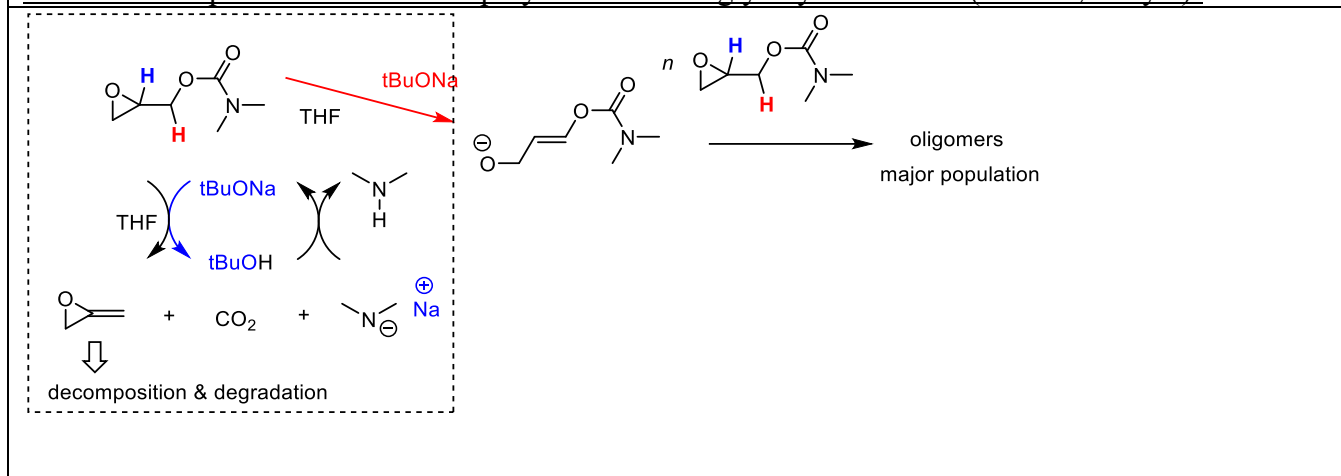
of the glycidyl carbamate was observed by $^1\text{H NMR}$, but no oligomer could be detected by MALDI-TOF such as entries 3 and 4.

Structure from transfer reaction (a)			Expected structure (b)			
DP	m/z (exp)	m/z (th.)	Structure	m/z (exp)	m/z (th.)	Structure
6	1038.6	1038.7	 <p style="text-align: right;">a₆</p>	967.5	967.5	 <p style="text-align: right;">b₆</p>
<p>Figure 1: MALDI-ToF spectrum of poly(glycidyl N,N-dimethylcarbamate) initiated with 12.5 mol% of t-BuONa (table 1, entry 5), corresponding structures and m/z for DP=6 and theoretical mass.</p>						

To better understand the process of polymerization, we analyzed the oligomers using MALDI-TOF in the reflectron mode (**Figure 1**). In this mode, we were able to determine that the expected oligomers obtained by initiation with $t\text{-BuO}^-$ correspond to the structures of the minor population b. The major population on the other hand actually corresponds to oligomers a where the effective initiator is generated through an elimination process (**Scheme 3**).

These results show that the t-BuOK and t-BuONa lead mainly to small chains induced by their strong basicity and the intrinsic reactivity of the monomer. Indeed, when compared to Stolarzewitz (glycidyl ether)²⁶ or Hans (glycidyl acetal),¹⁵ the glycidyl carbamate proved less prone to polymerizing. This might be due to an easier hydrogen abstraction of the monomer, which decreases the amount of either the available initiator or monomer (**Scheme 3**). Considering the proposed mechanism, the degradation and decomposition could even be catalytic.

Scheme 3: Proposed mechanism of polymerization of glycidyl carbamate (Table 1, entry 5).



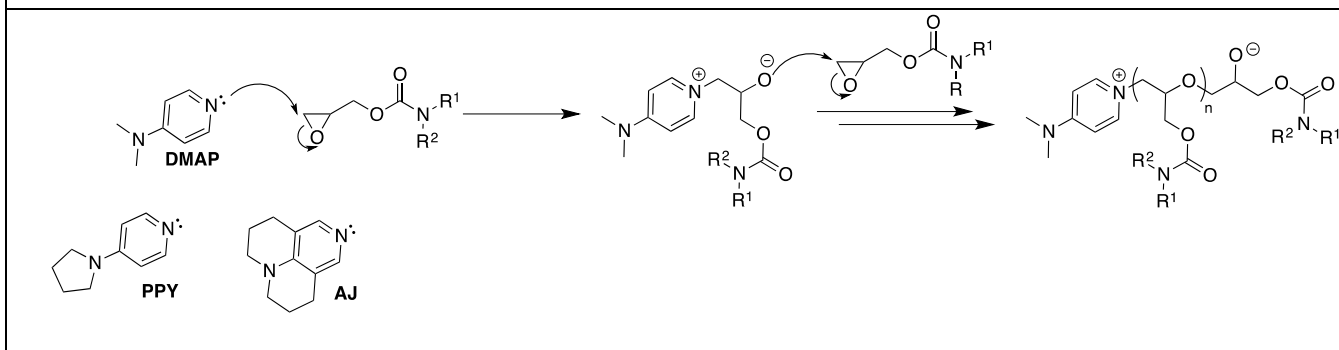
From these preliminary results, we suspected that, with a strong organic base and a very weak nucleophile, the degradation pathway was predominant. We thus turned our explorations toward more nucleophilic, yet less basic, systems.

Pyridine Derivatives as Initiators.

Three nonmetallic initiators exhibiting higher nucleophilicity and mild basicity were then selected. Among the various possibilities, the following nitrogen-based initiators were thus chosen: 4-N,N-dimethylaminopyridine (DMAP), 4-pyrrolidinopyridine (PPY), and 9-azajulolidine (AJ). These pyridine-derived catalysts are classically used in many reactions such as acylation (quite obviously for acetylation of alcohols), as well as alkylation,^{20,27} thanks to their enhanced nucleophilicity related to the donating ability of the exocyclic nitrogen atom that promotes the delocalization of electrons throughout the molecule.²⁸ Hence, they have gained interest in ring-opening polymerization of epoxides such as phenyl glycidyl ether or diglycidyl ether of bisphenol A²⁰ as an alternative route to organometallic catalysts. Even though the initiation step mechanism is not well-established, it is suggested that the active species are obtained by nucleophilic attack of the catalyst on the epoxide, thus generating a zwitterionic species with a positively charged nitrogen atom and a propagating alkoxide (**Scheme 4**). Furthermore, the moderate

pK_a of pyridine derivatives (9.71 for DMAP, 9.90 for PPY),²⁹ compared to alkali metal alkoxide such as *t*-BuOK (>16 for alkoxides) or P_4 -*t*bu (≈ 42.1 in acetonitrile), may prevent carbamate decomposition.³⁰

Scheme 4: Proposed mechanism of polymerization of glycidyl carbamate initiated by DMAP; structures of PPY and AJ.



To study the polymerization of the three glycidyl carbamates, (glycidyl *N,N*-dimethylcarbamate (GDMC, 1a), glycidyl *N*-piperidinylcarbamate (GPC, 1b), and glycidyl *N*-morpholinylcarbamate (GMC, 1c)), the two targeted degrees of polymerization of 20 and 40 were chosen ($[I]/[M] = 0.05$ and 0.025 , respectively). The reactions were performed under neat conditions at $50\text{ }^{\circ}\text{C}$. The conversion was followed by ^1H NMR spectroscopy looking at the disappearance of characteristic epoxide signals. All three initiators (i.e., DMAP, PPY, and AJ) were fully soluble in the monomers, and the reaction media started to get colored after about 1 h. **Table 2** presents the experimental conditions and results of polymerization of glycidyl carbamates using pyridine derivatives as initiators obtained by MALDI-TOF MS. Only the main populations observed by MALDI-TOF in the samples are reported in this table, except for **Table 2**, entries 1, 2, 3, 5, 7, and 13, where the three main populations' information are reported (more details can be found in the **Supporting Information** regarding the other distributions).

All of the reactions showed the disappearance of the monomer after 24 h at the ratio $[I]/[M] = 0.05$, as confirmed by ^1H NMR monitoring (**Table 2**, entries 1–18). However, decreasing the amount of the initiator to 2.5 mol % leads to traces of the monomer still remaining after 24 h. However, after 4 days (96 h), full conversion was achieved. Reactions lead to dark-brown resinous products.²⁰ The longer time

required to obtain full conversion might be due to a slower diffusion of the remaining monomers induced by the enhanced viscosity of the medium without the solvent.

The MALDI-TOF MS spectra and information (M_n , DP, and \bar{D}) obtained in linear and reflectron modes were used to elucidate the structure of the obtained poly(glycidyl carbamates) (**Table 2**). Similarly, as with strong base initiators, several populations with lower than expected M_n were also observed with the pyridine-based initiators. This suggests the presence of several chain-transfer reactions, thus limiting the molar masses obtained. To support the liability of MALDI-TOF MS results, SEC analyses were performed on different samples (**Table 2**, entries 1, 3, 5, 7, and 13). For the poly(glycidyl carbamates) initiated by DMAP at $[I]/[M]$ 0.05, \bar{D} for three populations obtained from MALDI-TOF MS analysis shows values between 1.06 and 1.20, in the range where molar mass values of polymers are still reliable using MALDI-TOF.³¹ The presence of multiple populations of different M_n within the same sample, still having \bar{D} within the same range (**Table 2** entries 1, 2, 3, 7, and 13, the three major populations reported), might be the reason for SEC results showing a higher \bar{D} (1.4–1.5) together with a slightly multimodal aspect of the SEC traces. The two techniques are complementary and orthogonal in describing the oligomers, but SEC relies on polymer properties that cannot be taken into consideration with MALDI-TOF. For instance, the major changes in the structure of the monomers GPC 1b and GMC 1c compared to GDMC 1a could induce fundamentally different hydrodynamic volumes and or interactions with the stationary phase for the corresponding oligomers in SEC. This leads to a reduced DP with this technique (value of 7, **Table 2**, entries 7 and 13 compared to the value of 10 for **Table 2**, entry 1), whereas MALDI-TOF results show homogeneous DP and \bar{D} for the three different oligomers, together with good confirmation of the polymer structure and accurate determination of absolute molecular weights of different populations of oligomers (polydispersity < 1.2).

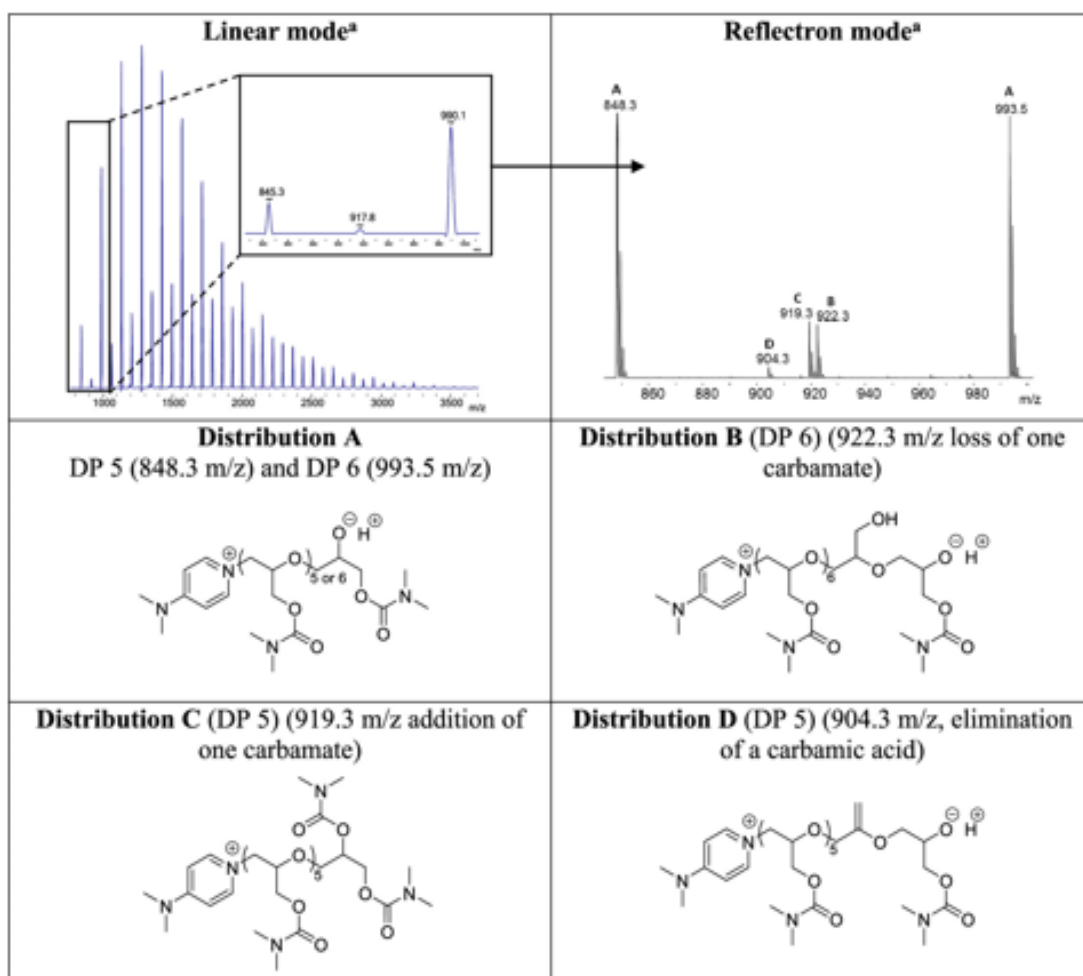


Figure 2: MALDI-ToF spectra of poly(glycidyl N,N-dimethylcarbamate), proposed structures for each population

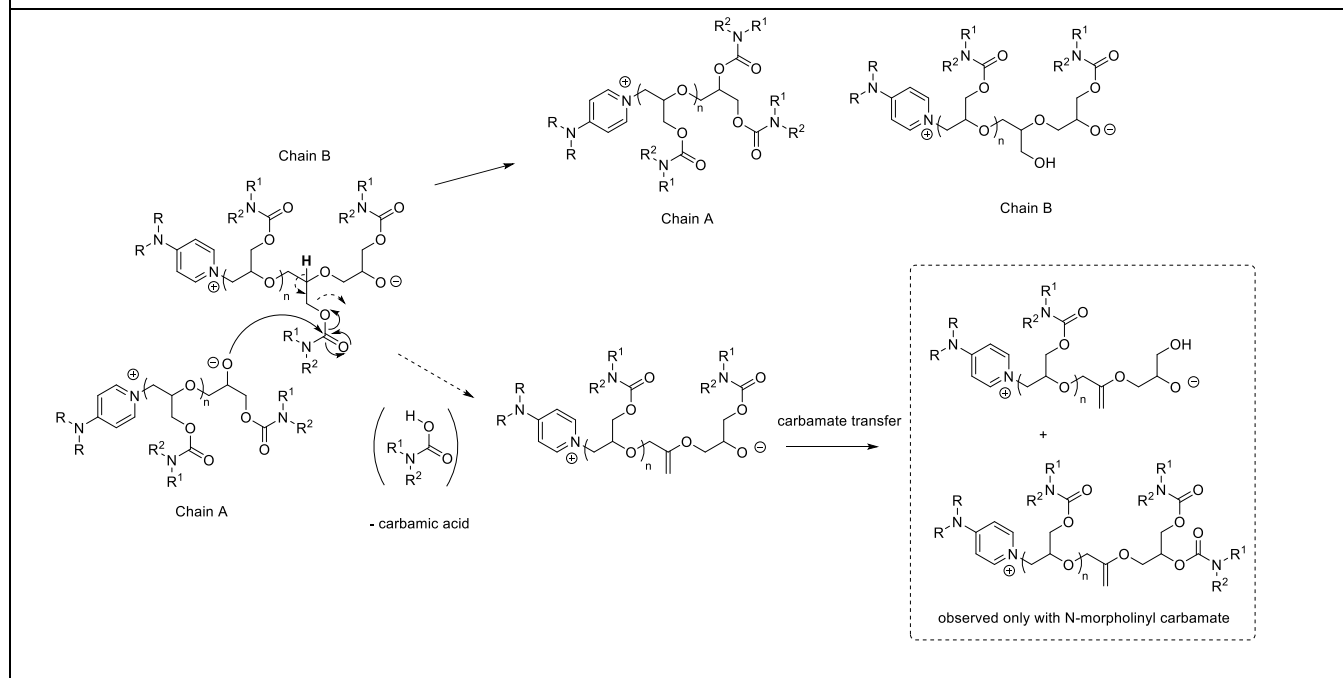
A case example of poly(glycidyl carbamate)'s MALDI-TOF spectrum is presented in **Figure 2**, referring to the polymerization of glycidyl N,N-dimethylcarbamate by DMAP (**Table 2**, entry 1). The linear mode shows two main distributions, and the difference between each peak on each population is 145.1 u, which corresponds to the mass of the monomer. The expected mass of the oligomer, if we considered a DP5 zwitterionic form cationized with Na⁺, is supposed to be 870.5 or 848.5 u if cationized with H⁺. The closest peak is located at 848.3 m/z (**distribution A**), which is in accordance with the last suggested specie. Using MALDI-TOF recorded in the reflectron mode, we were able to show that the second population

detected is in fact a combination of two distributions that differ by only 3 mass units, which we were not able to detect previously due to the peak width (**distributions B and C**). A last population was also detected, with a smaller intensity (**distribution D**). All of the described distributions are shown in **Figure 2**.

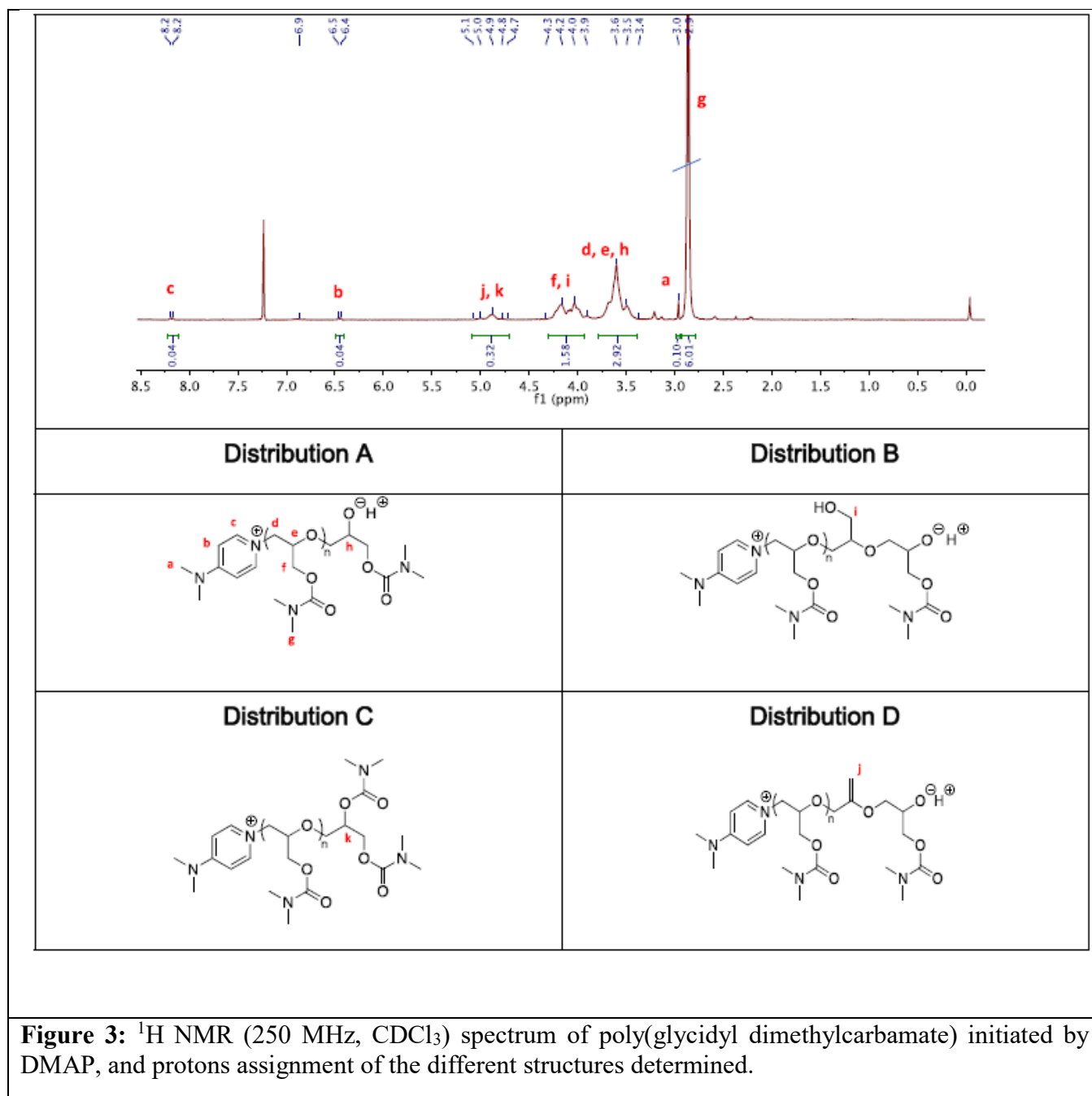
The sensitivity of the carbamate moiety combined with the transfer reactions we observed strongly suggests that nucleophilic attack might occur during the reaction because of the presence of the alcoholate propagating center and carbamates along the polymeric chain. The suspected fragments possibly lost are shown in **Scheme 5**. We can observe that the mass of **distribution B** corresponds to the mass of a chain that has lost one carbamate (-71.1 u) in the case of poly(glycidyl N,N-dimethylcarbamate). The simultaneous presence of both alcohol and alkoxide functions on one chain can lead to intramolecular proton exchange, thus creating several potential sites for chain growth. In that regard, branched polymers might be obtained since the propagation can occur on the backbone of the chain or on the newly generated alkoxide at the lateral chain from carbamate hydrolysis and then proton exchange. Such species have lower hydrodynamic radius compared to the linear counter- parts, which is suggested by the bimodal aspect of SEC traces. Furthermore, the transfer of carbamate from one chain to another theoretically leads to the addition of one carbamate moiety in the ω -end, which actually corresponds to the close- by population on the MALDI-TOF spectrum ($+71.1$ u), **distribution C**. Indeed, Hassouna et al.³⁰ have shown that carbamates in basic conditions may undergo a dissociation reaction leading to the release of an alkoxide. **Distribution D** corresponds to the loss of one carbamic acid moiety (-89.1 u), which is the result of commonly described transfer reactions with glycidyl monomers, and leads to the formation of a double bond in the chain²⁶ by proton abstraction. These observations are further supported by poly(glycidyl N-piperidinylcarbamate, GPC) or poly(glycidyl N-morpholinyl- carbamate, GMC) spectra, which show exactly similar distributions (see the **Supporting Information**, more specifi- cally **Table 2**, entry 13 in

details). However, these latter two monomers lead to more complex transfer reactions as several other distributions can be observed from the MALDI-TOF experiments, which are in fact the result of the combinations of aforementioned transfer reactions.

Scheme 5: Proposed mechanisms for the transfer reactions of carbamate during the polymerization of glycidyl (carbamate), using DMAP as initiator

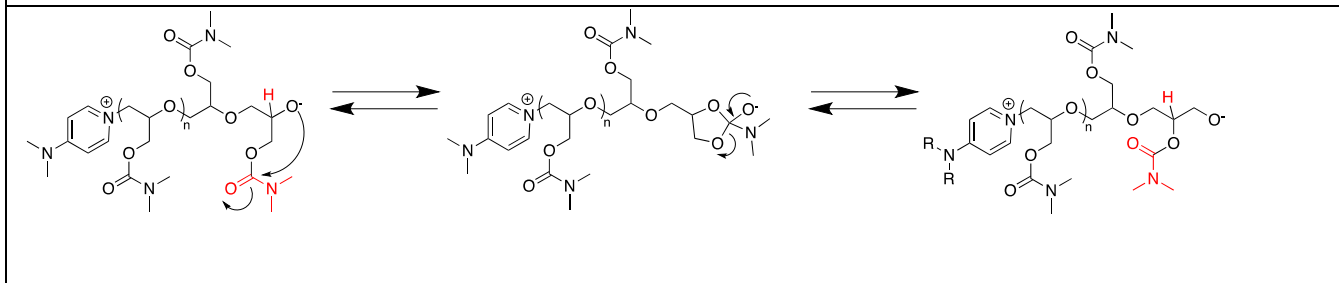


In **Scheme 5**, we propose three mechanisms to explain the different distributions. The alcoholate end chain acts as a nucleophile that can either attack the carbamate on the carbonyl, leading to the cleavage of the C-O single bond (plain arrow), or act as a strong base, thus abstracting the proton from the tertiary carbon on the polymer backbone (dotted arrow). Due to the presence of pyridine derivative initiators in the reaction medium, they are also potentially able to decompose the carbamate, leading to distribution B.



Nuclear magnetic resonance (NMR) spectroscopy supports the proposed mechanisms. The ^1H NMR spectrum of poly(glycidyl N,N-dimethylcarbamate) initiated by DMAP is presented in **Figure 3** with the assignment of the different observed protons.

Scheme 6: Proposed mechanism of intramolecular carbamate transfer in poly(glycidyl N,N-dimethylcarbamate) chain



Using ^{13}C NMR, we can find a signal at 72.5 ppm corresponding to a tertiary carbon, which correlates with a proton signal at 4.9 ppm in ^1H NMR (see the heteronuclear single quantum coherence (HSQC) spectrum in the **Supporting Information**). This proton is deshielded from 3.5 to 4.9 ppm, which can be attributed to the close proximity of the carbamate moiety (**Scheme 6**, proton k). This observation is in agreement with our previous work where it has been shown that this type of proton is indeed at around 5 ppm.²¹ The lower integration of this signal indicates that this transfer reaction is in minority, corresponding roughly between one-fourth and one-third of the oligomerization process. Whether this reaction principally happens intramolecularly or inter-molecularly is still uncertain, but we suggest a mechanism to obtain such intramolecular migration through a five-membered ring (**Scheme 6**). This mechanism has indeed been described by Garipov et al., where it was shown that a tetrahedral intermediate is formed through the reaction of a secondary amine with a carbonate moiety to release regioisomeric carbamate products.³²

Although the MALDI is a soft ionization technique leading to little in-source fragmentation, we suspect that carbamate cleavage is induced during the MALDI process. To further confirm the structures and invalidate the hypothesis of MALDI-TOF fragmentation, poly(glycidyl N,N-dimethylcarbamate) (Table 2, entry 2) was derivatized using 3-phenylpropionyl chloride under basic conditions. We observed the esterification of the free hydroxyl at the ω -end chain in the case of the main polymer distribution (distribution

A), from 1718.9 to 1851.1 m/z, in which the gain of a mass of 132.2 u corresponds to the addition of a 3-phenylpropionyl (3PP) moiety. In the case of polymer chains with one carbamate less (distribution B), two free hydroxyl groups are present, one at the ω -end chain and another at the lateral chain (**Figure 4**). In this case, two esters have effectively been incorporated, with a gain of 264.2 u. In the case of carbamate transfer at the ω -end chain (distribution C), no changes were observed as expected, since there is no available hydroxyl group.

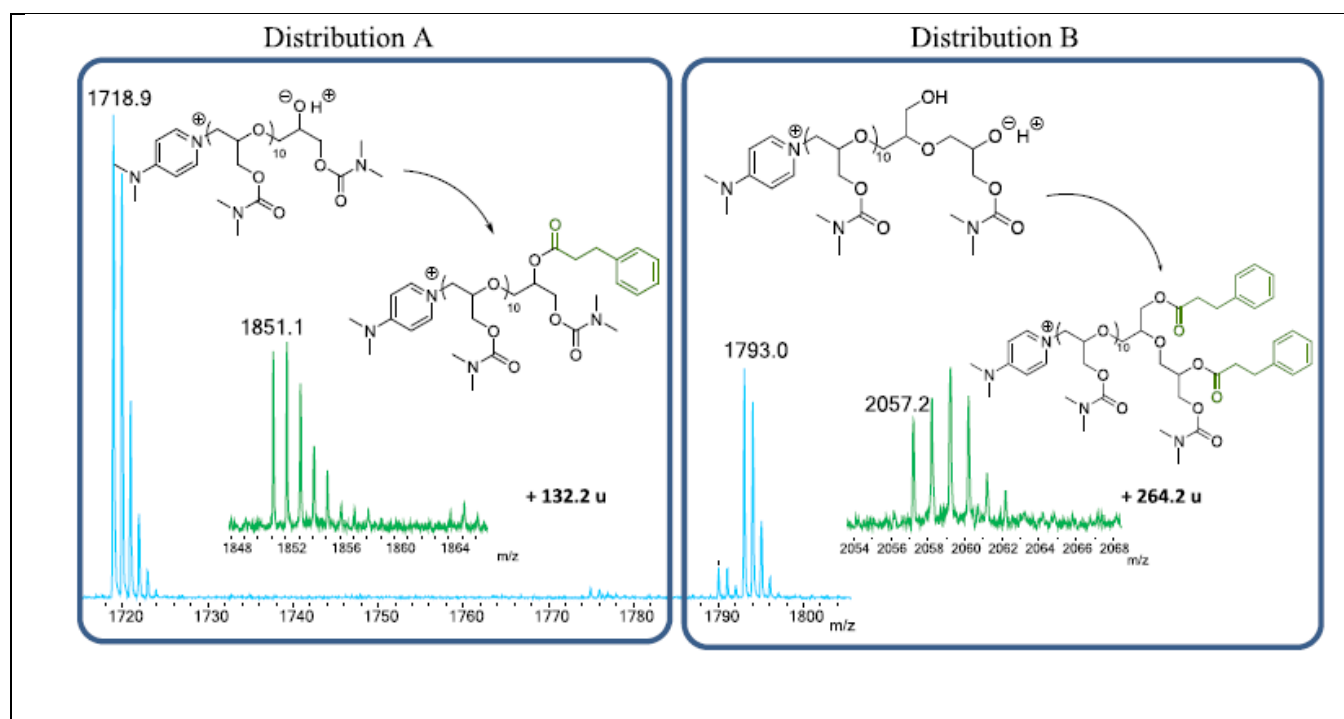


Figure 4. MALDI-TOF spectra recorded in the reflectron mode of poly(glycidyl N,N-dimethylcarbamate)_n [polymer n = X + H]⁺.

^a MALDI-ToF spectra before (blue) and after esterification (green) by 3-phenylpropionyl chloride for distributions A and B.

In summary, regarding the obtention of poly(glycidyl carbamates) using pyridine derivatives as initiators, no polymers with molecular weights higher than 3000 g·mol⁻¹ have been obtained. The use of these initiators has been motivated by their easy handling and constitute a starting point of the study of the

polymerization of glycidyl carbamates. However, in the light of obtained results, the molecular weights have to be increased to considerate real-life applications. Furthermore, we have shown that urethane sensitivity in anionic polymerization conditions may be a drawback if we consider potential copolymerization reactions with other monomers. Further studies will be conducted to decrease side-reactions on the urethane moiety by decreasing the alkoxyreactivity, leading to more controlled polymerization reactions and potential copolymerization with other epoxides.

Having in hand these original poly(glycidyl carbamates), we explored preliminary properties of these materials. Their affinity toward different solvents was determined for potential applications notably as film-forming agents.

Poly(glycidyl carbamate) Affinity with Solvents.

To highlight the differences in properties between the three poly(glycidyl carbamates) we previously synthesized (**Table 3**, entry 1 (p(GDMC)), entry 7 (p(GPC)), and entry 13 (p(GMC))), a study was conducted to determine the differences regarding their affinity toward solvents. The problematics of solvent selection for polymer applications is still a constant preoccupation in many fields such as biomedical or electronic devices and packaging. Indeed, the affinity of solvents toward polymers influences the solubilization, degradation, and stability of these materials in complex environments such as in painting or cosmetic formulas. This behavior of great importance is mostly driven by the interaction strength between these polymers and solvents. Hence, we have first considered Hansen's solubility parameters (HSPs) to approach the affinity between them. Then, the polymer-solvent affinities were experimentally investigated with a polymer thin film.

Polymer Solubility Using Hansen's Solubility Parameters (HSPs) and Flory–Huggins

Parameters χ . The values of δ_d (the dispersive component), δ_p (the polar component), and δ_h (the hydrogen-bonding component), the Hansen's solubility parameters, were theoretically calculated using the Hoftyzer and van Krevelen method. To do so, we determined the contributions of each structural group of the monomer unit using a group contribution method.³³ For each structural group, values of HSP components are attributed using tabulated values and the contributions of the structural group to the HSP components are estimated by multiplying these values by the number of occurrences of the structural group in the monomer unit. As an example, the detailed calculation of p(GDMC) (**Table 3**, entry 1) is presented in **Supporting Information**. The values of HSP of the three considered p(GC) are reported in **Table 3**. Then, the polymer–solvent affinity is evaluated from the difference between the HSP value of the considered polymer (P) and one of the solvents (S) of interest. This can be done by calculating the Flory–Huggins parameters $\chi_{P,S}$ (**eq 1**). When $\chi_{P,S} < 0.5$, the considered solvent has a good affinity for the polymer. When $\chi_{P,S} = 0.5$, the solubility is intermediate and is the limit of solubility, and for $\chi_{P,S} > 0.5$, the considered solvent is a nonsolvent.

$$\chi_{P,S} = \alpha \frac{V_s}{RT} \left[(\delta_{d,P} - \delta_{d,S})^2 + 0,25(\delta_{p,P} - \delta_{p,S})^2 + 0,25(\delta_{h,P} - \delta_{h,S})^2 \right] \quad (1)$$

where $\delta_{d,S}$ and $\delta_{d,P}$ are the HSP contributions of the dispersive forces; $\delta_{p,S}$ and $\delta_{p,P}$ are the HSP contributions of the polar interactions; and $\delta_{h,S}$ and $\delta_{h,P}$ are the HSP contributions of the hydrogen bonds of the polymer (P) and the solvent (S), respectively.

Table 3 : HSP of the 3 p(GC) δ_d : HSP dispersive component, δ_p : HSP polar component, δ_h : HSP hydrogen bonding component, δ_t : total HSP value calculated by $\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$				
	δ_d	δ_p	δ_h	δ_t
p(GDMC)	16.3	8.5	11.2	21.5
p(GMC)	18.2	8.0	11.4	22.9
p(GPC)	17.8	6.8	10.0	21.5

For the three considered p(GC), the values of $\chi_{p,s}$ are reported in Table 4. Apolar solvents such as toluene and cyclohexane are nonsolvent for p(GDMC) and p(GMC). Diethyl ether is a nonsolvent for p(GDMC) and p(GPC). For polar solvents and intermediate polarity ones, all three p(GC) have generally a good affinity with the majority of solvents.

Experimental Investigation of the Polymer–Solvent Affinity under Thin-Film Form.

To study the affinity between the p(GC) polymers and solvent using the smallest possible amount of product, we used thin films by depositing p(GC) on silicon substrates. In that regard, with only 2 mL of a 30 mg· mL⁻¹ p(GC) solution, we were able to run about 20 tests to apprehend the polymer–solvent affinities.

The polymer–solvent affinity can show specific behaviors that depend on the processing of polymers. Specifically, under the thin-film form, our previous work showed that polymer solubility with a solvent might deviate from its predicted solubility determined using $\chi_{p,s}$.³⁴ This can be attributed to the concentration of polymer in the film, which is generally above 20%, whereas the HSP generally reflects a situation where the concentration of the polymer is low.

Table 4 : Polymer-Solvent affinity classification									
	$\chi_{P,S}$			Dissolution test			Swelling test (SR)		
	p(GDMC)	p(GMC)	p(GPC)	p(GDMC)	p(GMC)	p(GPC)	p(GDMC)	p(GMC)	p(GPC)
Methanol	0.4	0.4	0.5				1.6	1.3	1.4
Ethanol	0.2	0.3	0.4				2.6	1.4	2.1
Isopropanol	0.2	0.2	0.3				1.6*	1.2	1.6
Ethyl acetate	0.2	0.3	0.2				1.9	1.7	1.9
Tetrahydrofuran	0.1	0.1	0				1.4	1.3	1.5
Acetone	0.1	0.2	0.2				*	2.2	2.2
Dichloromethane	0.2	0.1	0.1				1.5*	1.3*	1.4*
Diethyl ether	0.5	0.8	0.5				1.0	1.0	1.0
Toluene	1.0	0.9	0.6				1.3	1.2	1.4
Cyclohexane	0.8	1.3	1.0				1.0	1.0	1.0

The solvents are classified using the different criteria between -good solvents (green colored boxes): $\chi_{P,S} < 0.5$, total dissolution of the film for dissolution test and swelling ratio > 1.3 for swelling test, - intermediate solvents (yellow colored boxes) ($\chi_{P,S} = 0.5$, partial dissolution of the film for dissolution test and $SR = 1.3$ for swelling test) - non-solvents (red colored boxes) ($\chi_{P,S} > 0.5$, the film remains unchanged during the dissolution test and $SR < 1.3$ for swelling test. For swelling test, * indicates that the film is quickly deteriorated to the point that the thickness measurement fails.

In that regard, we deposited the three p(GC) on silicon substrates from a solution in dichloromethane as this solvent shows good solubility with the polymers and a fast evaporation rate. Fortunately, all three p(GC) showed good film-forming properties on silicon substrates, which leads to homogenous films (under optical microscopy observation) that persist for more than several weeks without any storage precaution. To study the affinity of these films with solvents, both solubility and swelling tests were performed. In solubility tests, one drop of solvent is deposited on the film, and whether there is film dissolution or not is an indicator of polymer-solvent affinity. If the film is totally dissolved, the solvent is a

good solvent of the polymer. If the film remains unchanged, the solvent is a nonsolvent of the polymer. If the film is partially dissolved, the solvent is an intermediate one. In swelling tests, the film is exposed to the solvent at a controlled partial pressure and the thickness of the film is recorded. The swelling ratio (SR) between the thicknesses of the film before and after swelling is in this case the indicator of polymer–solvent affinity. In a previous study, we have shown that the swelling ratio (SR) does not depend on the molar weight of the considered polymer. Furthermore, the partial pressure of 0.8 is a good compromise between a significant swelling of the film without systematic dewetting. As a general guideline, we considered that an SR ratio of 1.3 is the limit between a good solvent ($SR > 1.3$) and a nonsolvent ($SR < 1.3$).

Dissolution tests and swelling tests are presented in Table 4 and compared with the theoretical calculations for the three considered p(GC). First, most of the thin films of p(GDMC) are solubilized or at least deteriorated by deposition of polar solvents, and the swelling ratio is always above 1.3. In contrast, in the case of toluene and cyclohexane, which we considered to be nonsolvent according to the values of χ , the swellings of the films are less than 1.3, which confirms that there is very little affinity with these solvents. These observations are further supported by the fact that the films are weakly solubilized, which is indeed in good accordance with prediction. The results are similar to p(GPC), with the exception of toluene, which is a good solvent with regard to the two experimental tests. χ is however slightly above 0.5 but still close to that value. On the other hand, p(GMC) shows good correspondence for nonpolar solvents when comparing χ calculations, dissolution tests, and solvent swelling ratios but mixed results regarding polar solvents. In particular, solvents containing alcohol moieties show poor affinity during the dissolution and swelling tests, but the prediction using χ is always below 0.5. Overall, we tend to observe that p(GMC) exhibits lower swelling ratios compared to the other two p(GC). The differences between predicted solubility and experimental observations can be attributed to other factors that are related to the thin-film state: variation between diluted solutions (described by χ) and concentrated state of the thin film exposed

to solvent vapors may lead to unpredicted results. Furthermore, viscoelastic properties of the studied compound might also influence the behavior of the thin films.

Conclusions

We have shown that glycidyl carbamates can be polymerized in bulk conditions under organocatalysis conditions and without a solvent. The nucleophilicity of the initiator is mandatory, and simple pyridine derivatives were able to perform the oligomerization. However, the strong basicity of initiators mostly leads to undesired transfer reactions because of the presence of the carbamate moiety. The oligomers obtained have a maximum DP of 10–20 with masses up to 2000 g·mol⁻¹ for poly(glycidyl N,N-dimethylcarbamate), 2800 g·mol⁻¹ for poly(glycidyl N-piperidinylcarbamate), and 3700 g·mol⁻¹ for poly(glycidyl N-morpholinylcarbamate). The oligomer mixtures are indeed complex due to various transfers, migrations, and or elimination of the carbamate moieties, which make such oligomers difficult to analyze. However, the conditions proved compatible with the three glycidyl carbamates used and allowed the preparation under solvent-free conditions of an “oligo-urethane” based on linear oligoglycerol from biosourced monomers. Regarding the affinity of these new compounds with solvents, we have been able to predict their affinity with several solvents using the theory of Hansen’s solubility parameters, providing useful information for the manipulation of these materials. The results are globally in good agreement with experimental tests on these p(GC) thin films. Thus, we have shown here that the method we have developed in a previous work and applied in this article is suitable to investigate the affinity of p(GC) with solvents.³⁴ Extension of this work is currently ongoing in our groups, looking at the optimization of the polymerization methods and the characterization of these novel oligomers to determine their properties, and will be reported in due course.

1	GDMC 1a	DMAP	0.05	24	>99	3025	20	1670	11	1460 Đ = 1.4
2			0.025	72	97	5750	40	1870	13	
3		PPY	0.05	24	>99	3050	20	1600	11	1580 Đ = 1.4
4			0.025	72	>99	5950	40	1850	13	
5		AJ	0.05	24	>99	3075	20	1630	11	2300 Đ = 1.6
6			0.025	24	>99	5975	40	1860	13	
7	GPC 1b	DMAP	0.05	24	>99	3825	20	1400	10	1400 Đ = 1.4
8			0.025	-	-	7525	40	2580	14	
9		PPY	0.05	24	>99	3850	20	2050	11	-
10			0.025	24	97	7325	40	2800	15	
11		AJ	0.05	24	>99	3875	20	1830	10	-
12			0.025	24	97	7350	40	2570	14	
13	GMC 1c	DMAP	0.05	24	>99	3850	20	2170	11	1425
14			0.025	degradation	7600	40	2290	12		
15		PPY	0.05	24	99	3900	20	1850	10	-
16			0.025	96	>99	7650	40	2420	13	
17		AJ	0.05	24	>99	3925	20	2240	12	-
18			0.025	96	>99	7675	40	2470	13	
								2670	14	
								3010	16	
								2830	14	
								3660	19 ^c	
								1740	9	
								1940	10	
								2350	12	
								2660	14	

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