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Non isocyanate route to polyurethanes from polyglycerol five membered polycarbonate

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Abstract

Polyglycerol five membered cyclic carbonate (CPG3) was synthesized from polyglycerol, a by-product of bio-diesel production and dimethyl carbonate (DMC). CPG3 react easily with amines to yield urethane bond using a totally free isocyanate synthetic way. The use of different di and tri-amines allows the formation of polyurethanes with potential broad range of applications. The renewable origin of polyglycerol, the low toxicity of dimethyl carbonate and the experimental conditions developed involving reactions performed in good yield without solvent and without formation of by-products allow envisaging a completely green synthesis of polyurethanes.The aim behind creating polyurethane without using isocyanates has been reached, hence stressing the effectiveness of our approach. In fact, we managed to develop a biocide-free synthesis process by relying on green chemical products such as polygluceril and the dimethyle carbonate. Likewise, this process offers a very important advantage concerning the treatment that we aim to develop so as to treat wood then move on to aqueous stage.

Keywords: glycerol carbonate / polyglycerol / polymerization, polyurethanes

1. Introduction

Polyurethanes, a versatile class of polymers are useful for a wide range of applications like foams, coatings, adhesives, sealants and elastomers **[1,2]**. Polyurethanes are generally produced by reaction of di or poly-functional isocyantes with diols or polyols. However isocyanates are hazardous due to their reactivity, toxicity and mode of production involving most of the time phosgenation reactions. Non isocyanate synthesis of polyurethanes is therefore of great interest for the development of more environmentally acceptable alternatives. Recently, several articles have described the reaction of amines with five membered cyclic carbonates leading to hydroxy-urethanes or polyurethanes **[3-6]**. In this context, phenoxycarbonyloxymethylethylene carbonate has been described as a valuable intermediate to obtain polyurethanes by reaction with different diamines **[7]**. The aim of this paper is to report a novel way of producing polyurethanes from polyglycerol five membered polycarbonates (CPG3). Indeed CPG3 obtained from polyglycerol and dimethyl carbonate, are used in polycondensation reaction to prepare polyurethanes. The interest of this approach lies not only in the fact that it is completely free from the use of isocyanates, but also allows valorization of glycerol a by-product of biodiesel production. In addition, polyglycerol and dimethyl carbonate are both recognised as green chemicals allowing to envisage additional environmental benefits **[8 -12]**.

2. Materials and methods

2.1. Materials

Dimethyl carbonate (DMC), butylamine, N,N-ethylenediamine were purchased from Fluka-Sigma-Aldrich Chimie SARL (St Quentin Fallavier, France). Polyglycerol was obtained from Novance (Compiègne, France) as a mixture of compounds with an average molecular weight of 242 (n ~ 3).

2.2. Instruments

The spectra RMN ^{1}H ^{13}C in liquid stage have been recorded on a chemical spectrometer Bruker DRX 400at a resonance frequency of 400 MHZ, the chemical movements are partially expressed by million(ppm). The following abbreviations have been used to describe the various signs: s for singlet, d for doublet, dd for double doublet, t for triplet, and m for multiplet. Different deuterated solvents have been used according to the solubility of the analyzed components. Their specific nature is specified as the case may be. The infrared absorption spectra have been recorded on a spectrometer FTIR Perkin Elmer spectrum 1000 from a film put between two pastilles of NaCl for the liquid products and as a pastille of KBr for the solid products. The typical bands of the products are expressed in cm^{-1}.

2.3. Products

The products as well as the chemical reactives used during this study originated from firms such as Acros Organics (Noisy le grand, France) and Fluka- sigma- Aldrich SARL, (st Quentin Fallavier, France). The industrial products have been supplied by Novance: the glycerol carbonate, the glycerol, the polyglocerol PG3.

2.4. Solvents

Some solvents have been purchased rather anhydrous in order to be used right away, namely: Pyridine, Methanol, and the Toluene (Ridel De Haen) Others have been purified and dried through distillation, the dichloromethane on P2 O5 and DMF CaH2 then maintained on a molecular sieve.

2.5. Synthesis of polyglycerol carbonate

In a 100 mL round bottomed flask equipped with a magnetic stirrer, a condenser and a thermometer, polyglycerol (2.10 g, 8.6 mmol), dimethyl carbonate (1.55 g, 17.2 mmol) and K_2CO_3 as catalyst (60 mg, 0.43 mmol) were placed. The reaction was carried out under reflux for 5 h. Methanol and residual DMC were then evaporated under reduced pressure.

^{1}H NMR (400 MHz, DMSO-d6),δ(ppm): 4.89 (m, 2H); 4.81-4.77 (broad s, OH); 4.51 (m, 2H); 4.28 (m, 2H); 3.78-3.16 (m, polyglycerol protons)

FTIR$\nu_{C=O}$(NaCl film):3458 cm^{-1} (broad, OH); 2983 cm^{-1} (C-H aliphatic); 1781 cm^{-1} (C=O cyclic carbonate); 1750 cm^{-1} (C=O acyclic carbonate); 1403 cm^{-1} (low, CH_2); 1181 cm^{-1} (low, CH); 1054cm^{-1} (low, OH).

2.6. Reaction with amines

Five membered cyclic carbonate of polyglycerol was mixed with amine at room temperature in a round bottomed flask equipped with a magnetic stirrer. Progress of the reaction was monitored by FTIR spectroscopy following the disappearance of the cyclic carbonyl band at 1790 cm^{-1}.

2.7. Gel Permeation Chromatography

Molecular weight distribution of polyurethanes was analyzed by gel permeation chromatography with respect to poly(ethylene glycol) standards using a Styragel HR1 column. Samples were dissolved in DMF at a concentration of 2.0 % and the injection volume equal to 20 μL. Elution was performed at 40°C using N,N-dimethylformamide at a flow rate of 1.0 mL mn^{-1}. On a thin layer: they are carried out on a sheet of silice Merck (5535) Kiesel Gel 60F254 then exposed to sulfuric acid, the eluant is specified for each analysis. Using the silice gel on a column 60 Merck (7737) having a granulatometry between 0.040 and 0.063 mm.

3. Results and discussion

Similar to the results reported by Rokicki concerning preparation of glycerol carbonate, synthesis of polyglycerol carbonate was realized using dimethyl carbonate (DMC) **[13-19]**. Polyglycerol (PG3) used during this study was produced by Novance under basic catalysis and consisted of a mixture of oligomers with an average degree of polymerization of 3. Based on a theorical molecular weight of 242 corresponding to a linear triglycerol, PG3 was reacted with different amounts of DMC in the presence of K_2CO_3 as catalyst (figure 1). Reaction was carried out without solvent under reflux for 5 h.

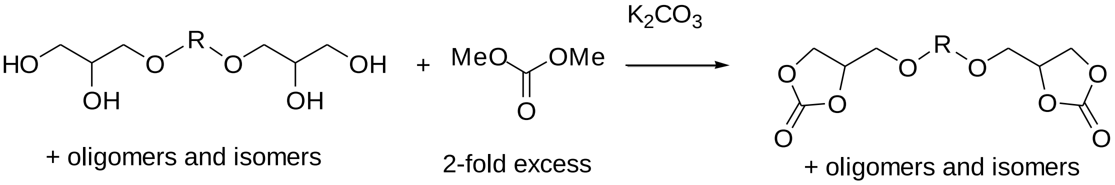


Figure 1: Reaction of PG3 mixture with DMC

Figures 2 and 3 represent FTIR and ^{1}HNMR analysis of the crude reaction product after evaporation of methanol and residual DMC.

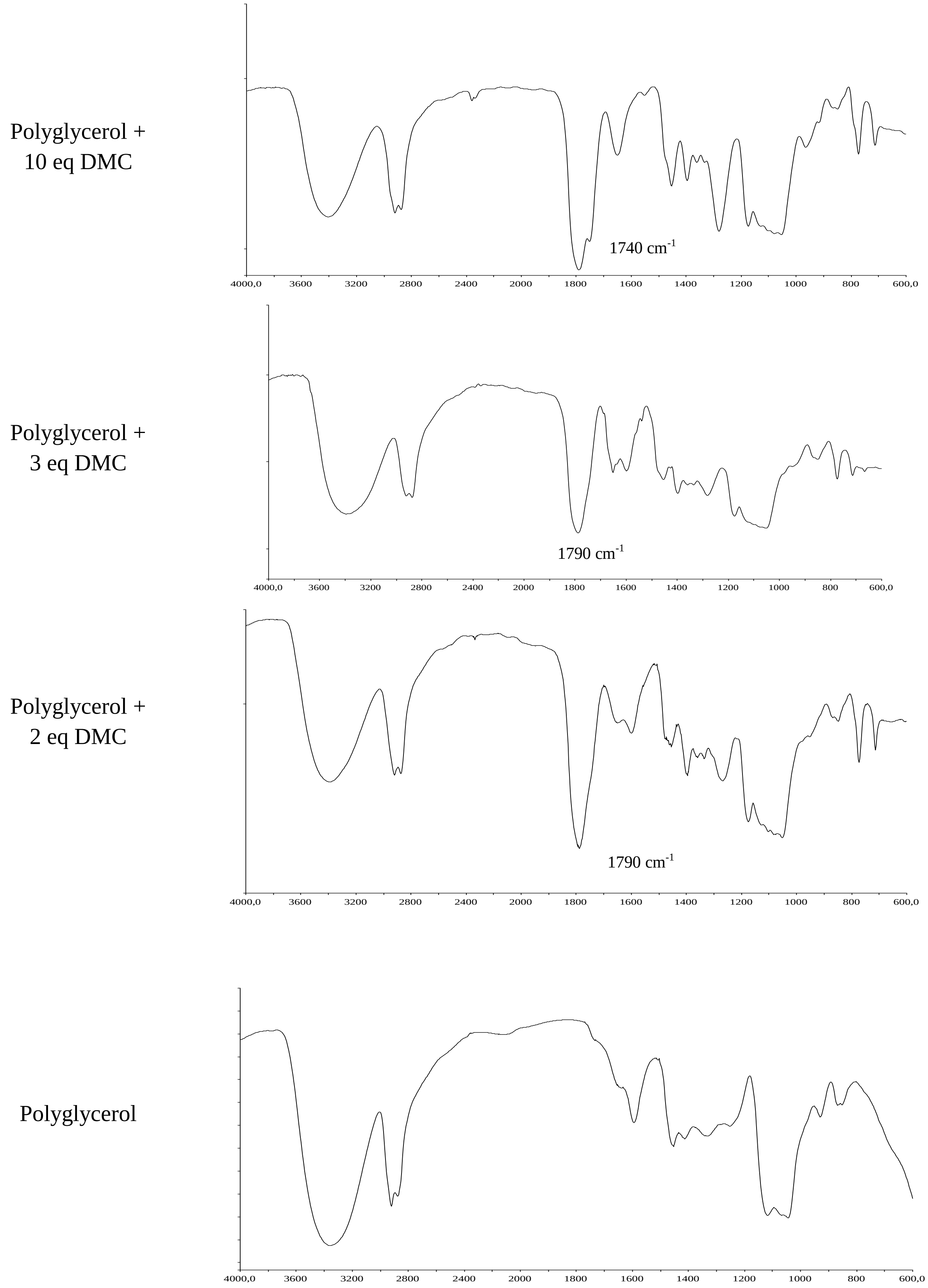


Figure 2: FTIR spectra of reaction product of PG3 with different amount of DMC

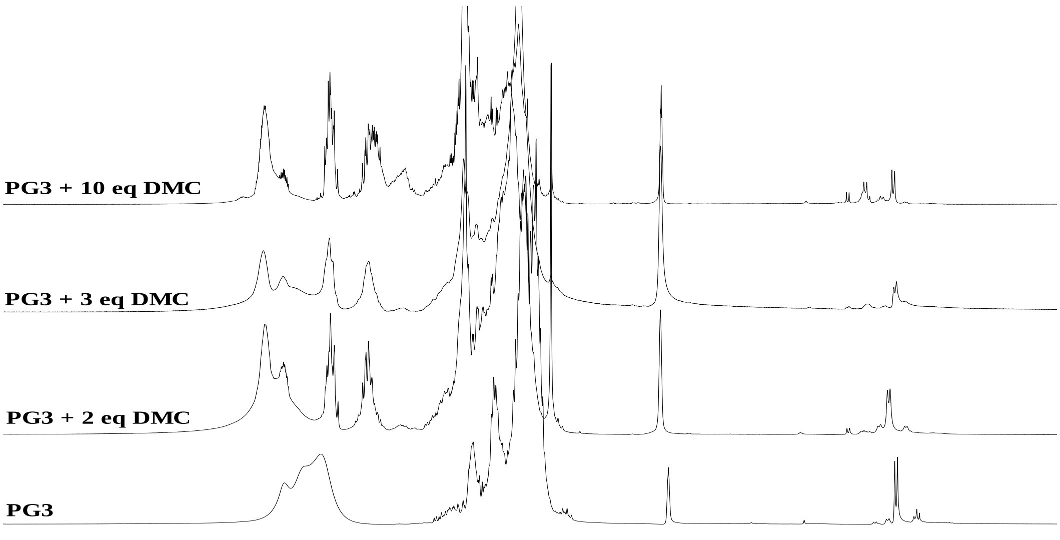
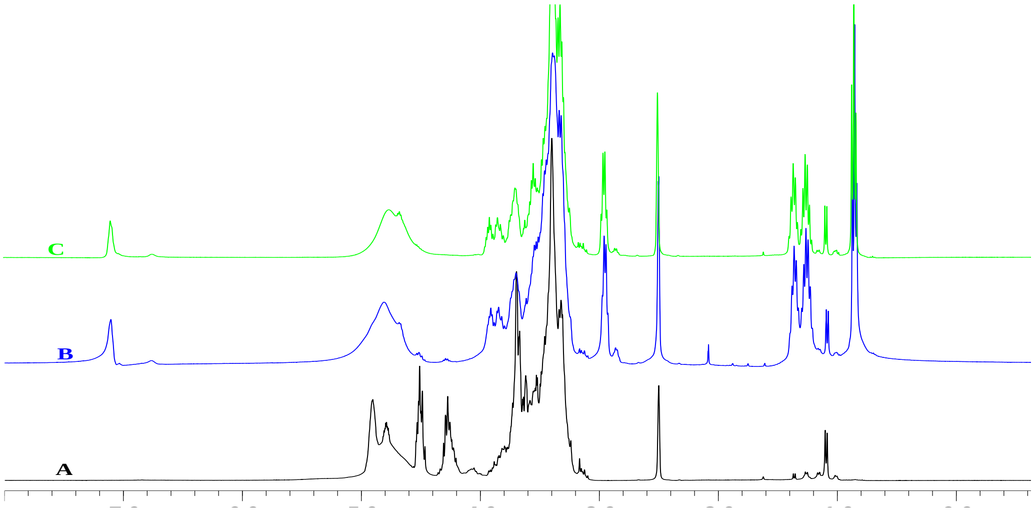


Figure 3: ^{1}H NMR spectra of reaction product of PG3 with different amount of DMC (DMSO d-6, 400 MHz)

The use of 2 or 3 equivalents of DMC calculated on the basis of an average theoretical molecular weight of 242 leads mainly to the formation of five membered cyclic carbonate as demonstrated by the characteristic carbonyl absorption band at 1790 cm^{-1} (figure 2). At the same time, 1H NMR spectra indicate characteristic signals for protons of the five membered cyclic carbonate appearing at 4.89, 4.51 and 4.28 ppm explained by reaction of DMC with vicinal OH groups of PG3 (figure 2). The use of larger amount of DMC (10 fold-excess) leads to the formation of cyclic and acyclic carbonates characterized by two infra red absorption bands at 1740 and 1790 cm^{-1} characteristic of carbonyl group of the linear and cyclic carbonates respectively. Residual absorption band in the region of 3400 to 3600 cm^{-1} indicated that some hydroxyl groups are still present at the end of the reaction even if DMC was used in excess. Formation of acyclic carbonate is demonstrated by the appearance of a new signal at 4.08 ppm ascribable to hydrogen atoms at proximity of acyclic carbonate moiety in the NMR spectrum. Reactivity of CPG3 was then investigated with n-butylamine choose as model compound to optimize reaction conditions. n-butylamine without solvent reacts readily with CPG3 at room temperature as demonstrated by the rapid disappearance of the carbonyl cyclic carbonate band at 1790 cm^{-1} associated with the appearance of a new absorption band at 1740 cm^{-1} characteristic of the carbonyl group of the carbamate function. Reaction can also be carried out in water due to the higher nucleophility of amine (figure 4).



(A) CPG3, (B) CPG3 + n-butylamine without solvent, (C) CPG3 + n-butylamine in water

Figure 4: ^{1}H NMR spectra of reaction of CPG3 with n-butylamine (DMSO d-6, 400 MHz)

To evaluate more precisely the amount of cyclic carbonate present on the CPG3, different amounts of n-butylamine were reacted with a known amount of CPG3 obtained after reaction of 2 equivalent of DMC. Results are reported in table 1.

The quantity of cyclic carbonate present on CPG3 is lower than the expected calculated value according to the theoretical molecular weight. Indeed, the measured value of cyclic carbonate present in CPG3 is comprised between 4.7 and 5.3 meq/g, while estimated value on the basis of a dicarbonate obtained from a linear triglycerol should be of 6.8 meq/g.

Table 1: Reaction of polyglycerol carbonate with different amount of n-butylamine

entry	n-Butylamine (eq) [1]	Weight Gain (%)	Cyclic carbonate (meq/g of CPG3)	$\nu_{C=O}$ 1793 cm^{-1}	$\nu_{C=O}$ 1704 cm^{-1}
a	0.5	12.5	1.7	yes	yes
b	1	21.5	3.0	yes	yes
c	1.25	33.5	4.7	yes	yes
d	1.5	37.5	5.3	no	yes
e	2	43	6.1	no	yes
	4	42.5	6.0	no	yes

[1] calculated on the basis of a dicarbonate of PG3 with an average molecular weight of 294

Reativity of CPG3 was further investigated with different diamines or triamines like ethylenediamine, butylenediamine, hexamethylenediamine, lysine monohydrate and diethylenetriamine. All reactions were performed at room temperature without solvent with an equimolar ratio of CPG3 and diamine, except in the case of lysine monohydrate, where the mixture was heated at 50°C to allow solubilization of the product. Formation of polyurethane is demonstrated as previoulsly by FTIR and ^{1}HNMR analyses. Gel permeation chromatography indicates formation of poly-condensation products with molecular weights comprised between1500g/mole to 2000g/mole, while molecular weights of starting oligomers are comprised between 400g/mole to 500g/mole. FTIR analyses indicate disappearance of carbonyl band of cyclic carbonate function associated with appearance of a new absorption band at 1740 cm^{-1}. In the same time, ^{1}H NMR spectra indicate as previously observed with n-butylamine disappearance of characteristic signals of protons of the five membered cyclic carbonate and appearance of characteristic NH signal of the carbamate function around 7 ppm.

Conclusion

Results indicated clearly that five membered cyclic carbonate of polyglycerol could be a valuable intermediate for the synthesis of polyurethanes. CPG3 is synthesized easily from environmentally friendly dimethyl carbonate andpolyglycerol resulting from oligomerisation of glycerol obtained as a by-product of biodiesel production. The use of different diamines or triamines leads to the corresponding polyurethanes using a totally free isocyanate synthetic way which can find a broad range of application. In addition to the renewable origin of polyglycerol, the use of naturally occurring amino acid like lysine allows to envisage a completely green synthesis of polyurethane. Such compounds constitute a valuable alternative of valorization of glycerol resulting from the increasing production of biodiesel. Further experiments are however necessary to investigate more deeply the potential of such approaches.

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