

Microwave-Assisted Synthesis of Polyglycerol from Glycerol Carbonate

Kamal Iaych,¹ Stéphane Dumarçay,¹ Emmanuel Fredon,¹ Christine Gérardin,¹ Alain Lemor,² Philippe Gérardin¹

¹Laboratoire d'Etudes et de Recherche sur le Matériau Bois, EA 4370, Nancy Université, Faculté des Sciences et Techniques, BP 70239, 54506 Vandoeuvre lès Nancy, France

²Novance, BP 629, 60206 Compiègne, France

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ABSTRACT: Microwave irradiation of glycerol carbonate allows formation of glycidol, which readily polymerizes to form polyglycerol under mild conditions comparatively to the classical polyetherification reaction involving high temperature and basic conditions. Analysis of the crude reaction mixture indicated the presence of low-molecular weight oligomers constituted mainly of di, tri, and tetraglycerols with small quantities of higher molecular weights oligomers. Molecular size distribution was relatively similar to that of polyglycerols obtained under basic condition, even if these latter

contained slightly higher amounts of high-molecular weight oligomers. Structure of oligomers differs slightly according to the conditions of polymerization, and polyglycerols are obtained under microwave activation containing higher contents of cyclic isomers, whereas polyglycerols obtained under basic conditions contain more ramified isomers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2354–2360, 2011

Key words: glycerol carbonate; polyglycerol; polymerization; microwaves

INTRODUCTION

Glycerol is a versatile renewable raw material, which can be obtained from glucose fermentation, sorbitol hydrogenolysis, or as a by-product of biodiesel production from the transesterification of plant oils and animal fats.¹ Because of the increasing production of biodiesel during the last decade, the availability of glycerol has greatly increased justifying the development of specific applications for its valorization. Several applications have been evaluated over the past years leading to different review papers devoted to this emerging topic.^{2–5} Among these, polyglycerols, consisting mainly of low-molecular weight glycerol oligomers, have received a lot of attention as hydrophilic component for neutral surfactants and emulsifiers for food cosmetic and pharmacy.⁶ Polyglycerols have also been investigated to improve wood-dimensional stability due to their ability to diffuse

through the cell walls and their capacity to interact with wood-cell-wall polymers preventing shrinking on drying.^{7,8} Up to now, synthesis of polyglycerols from glycerol involves either drastic conditions based on high temperature and alkaline conditions providing complex mixtures of oligomers with no well-defined chemical composition,^{9,10} or more elaborated regioselective methods leading to polyglycerol oligomers of well-defined structure.¹¹ Glycerol carbonate, easily synthesized on industrial scale by Novance, using an environmental friendly inexpensive process consisting of a carbamoylation–carbonation reaction between urea and glycerol in presence of a Lewis acid catalyst,^{12,13} can be considered as an alternative starting material to prepare new polymeric materials. Hyperbranched aliphatic polyethers were recently obtained by self-condensation of glycerol carbonate showing that, like glycidol, the cyclic carbonate could serve as a source of new polymeric materials.¹⁴ Moreover, glycerol carbonate was shown to undergo decarboxylation under distillation leading to glycidol,¹⁵ which can be subjected to further polymerization similarly to the reactions described in the formation of hyperbranched polyglycerol.^{16,17} Another possibility of polymerization is based on nucleophilicity of primary hydroxyl group of glycerol carbonate, which can react with tetrahedral sp³ carbon of cyclic carbonate to form ether linkage or with trigonal sp² carbon to form carbonate linkage. The present article describes preliminary results concerning polymerization of glycerol

Correspondence to: P. Gérardin (gerardin@lermab.uhp-nancy.fr).

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carbonate using different experimental conditions and especially the advantages of microwaves heating compared to conventional thermal heating in such reactions.

EXPERIMENTAL

General

All reagents were purchased from Acros Organics (Noisy le Grand, France) or from Sigma-Aldrich SARL (St Quentin Fallavier, France). Solvents and reagents were purchased from Acros Organics (Noisy le Grand, France) and used without further purification. Glycerol carbonate and polyglycerol of industrial grades were obtained from Novance (Compiègne, France). Polyglycerol consists of a mixture of compounds with an average molecular weight of 242 ($n \sim 3$). Glycerol carbonate was synthesized by Novance using recently patented environmental friendly process described earlier.¹⁰ Industrial grade glycerol carbonate was purified from residual glycerol by distillation under vacuum before use (bp 125–130°C, at 4 mbar). Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed with a TG-DTA 92-16 Setaram Instrument. The sample was heated from 20 to 500°C at a rate of 6°C/min under air in Al₂O₃ crucible. NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ with a Bruker DRX 400 spectrometer (400 MHz for ¹H and 100 MHz ¹³C). Chemical shifts are expressed in ppm. FTIR spectra were recorded as thin films between NaCl plates on a Perkin-Elmer FTIR spectrometer SPECTRUM 2000.

Synthesis of polyglycerol under microwave activation

MW irradiation was performed in a single-mode focused CEM reactor (Model Discover, CEM Co., Matthew, NC) operating at 2.45 GHz with ability to control output power. Freshly distilled glycerol carbonate (500 mg) was placed and in a closed 10-mL tube and heated under microwaves for different times and power (see table). Polyglycerol was obtained without further purification.

Synthesis of linear oligomers

(D,L- α,β -Isopropylidenglycerol) tosylate (solketal tosylate) (1)

Tosyl chloride (6.9 g and 0.60 mmol), dissolved in dichloromethane (50 mL), was added dropwise at 0°C to a mixture of solketal (4.0 g and 30.26 mmol), triethylamine (3.6 g and 36.27 mmol), and 4-dimethylaminopyridine (73 mg, 0.60 mmol) solubilized in dichloromethane (15 mL). After stirring at room temperature for 16 h, the crude reactional mixture was washed successively with 5% aq. HCl (50 mL), 5% aq.

NaHCO₃ (50 mL), dried with MgSO₄, and concentrated under reduced pressure. Product thus obtained was recrystallized in hexane to yield 1 (70%).

¹H NMR (CDCl₃): δ = 1.31 (s, 3H); 1.34 (s, 3H); 2.45 (s, 3H); 3.76 (dd, 1H); 3.95–4.05 (m, 3H); 4.25 (m, 1H); 7.34 (d, 2H); 7.80 (d, 2H).

¹³C NMR (CDCl₃): δ = 21.6 (1C); 25.1 (1C); 26.5 (1C); 66.3 (1C); 69.4 (1C); 72.7 (1C); 109.9 (1C); 127.9 (2C); 129.8 (2C); 132.5; 145.0 (1C).

Linear diglycerol (3)

Solketal (1.61 g and 12.21 mmol), solubilized in dry DMF (50 mL), was added dropwise under nitrogen to sodium hydride 60% dispersion in mineral oil prealably washed with dry THF (500 mg and 12.5 mmol). After stirring at room temperature for 1 h, tetrabutylammonium bromide (378 mg and 1.17 mmol) and solketal tosylate (1) (5.10 g and 17.81 mmol), diluted in dry DMF (25 mL), were added, and the resulting mixture was stirred for 16 h under nitrogen. Water (20 mL) and diethylether (20 mL) were added to the reactional mixture, and the organic phase was separated. Aqueous phase was extracted again with diethylether (2–20 mL). Organic phases were mixed together, dried with MgSO₄, and concentrated under reduced pressure to yield 2 (52%). Removal of acetal was carried out in refluxing methanol in the presence of Dowex 50WX8 acidic resin. Diglycerol (3) thus obtained was purified by column chromatography with dichloromethane/methanol (8/2) as eluent (82%).

¹³C NMR (DMSO-*d*₆): δ = 63.5 (2C); 70.9 (2C); 73.7 (2C).

Linear triglycerol (6)

Solketal (5.02 g and 38.06 mmol) and tetrabutylammonium bromide (613 mg and 1.9 mmol), dissolved in *n*-hexane (25 mL), were mixed with 50% aq. solution of NaOH (5 mL). Epichlorhydrin (7.04 g and 76.1 mmol), dissolved in hexane (5 mL), was then added, and the resulting mixture was vigorously stirred at 80°C for 2 h. The mixture was diluted with water (20 mL) and extracted with diethylether (2 \times 20 mL). The combined organic extracts were dried with MgSO₄ and concentrated under reduced pressure to yield 4 (66%).

Compound 4 (6.03 g and 32.04 mmol) thus obtained, dissolved in hexane (5 mL), was then added dropwise at 60°C to a mixture of solketal (5.02 g and 38.06 mmol), tetrabutylammonium bromide (0.61 g and 1.89 mmol) dissolved in hexane (25 mL), and 50% aq. solution of NaOH (25 mL). The resulting mixture was vigorously stirred at 60°C during 4 h. The mixture was diluted with water (20 mL) and extracted with diethylether (2 \times 20 mL).

The combined organic extracts were dried with MgSO_4 and concentrated under reduced pressure to yield **5** (47%). Removal of acetal groups was carried out in refluxing methanol in the presence of Dowex 50WX8 acidic resin for 16 h. Resin was removed by filtration, and the filtrate was concentrated under reduced pressure. Final purification of triglycerol (**6**) was carried out by removal of the excess of solketal by distillation using a Kugelrohr Apparatus (45%).

^{13}C NMR(DMSO- d_6): $\delta = 63.1(2\text{C}); 68.8(1\text{C}); 70.6(2\text{C}); 72.8(2\text{C}); 72.9(2\text{C})$

1,2:6,7-Diepoxy-4-oxaheptane (**7**):

m-CPBA 70% (10.6 g and 63 mmol), dissolved in dichloromethane (100 mL), was added dropwise to allyl glycidyl ether (5 mL and 42.1 mmol) in dichloromethane (10 mL). After stirring at room temperature for 24 h, 1M $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) was added, the organic layer separated, and the resulting aqueous layer was extracted with dichloromethane (2×50 mL). The combined extracts were washed with 0.5M NaOH, dried with MgSO_4 , and concentrated to yield **7** as a colorless oil (79%).

^1H NMR (CDCl_3): $\delta = 2.63$ (m, 2 H); 2.78 (m, 2 H); 3.20 (m, 2 H); 3.45 (m, 2 H); 3.80 (m, 2 H).

^{13}C NMR(CDCl_3): $\delta = 44.1(2\text{C}); 50.8(2\text{C}); 72.0(2\text{C})$

Linear tetraglycerol (**9**):

Solketal (1.61 g and 12.21 mmol) and tetrabutylammonium bromide (196 mg and 0.6 mmol), dissolved in *n*-hexane (5 mL), were mixed with 50% aq. solution of NaOH (5mL). Compound **7** (320 mg and 2.4 mmol) was then added under vigorous stirring at 80°C. After 4 h, the mixture was diluted with water (20 mL) and extracted with ethyl acetate (2×20 mL). The organic extracts were washed with brine, dried with MgSO_4 , and concentrated under reduced pressure. Excess of solketal was removed by distillation using a Kugelrohr Apparatus. Product was purified by column chromatography using dichloromethane/acetone (7/3) as eluent to yield **8** (38%). Compound **8** was stirred overnight in refluxing methanol in the presence of Dowex 50WX8 acidic resin. The resin was then removed by filtration, and the filtrate was concentrated and purified by column chromatography [dichloromethane/methanol (7 : 3) to yield tetraglycerol **9** (70%)].

^{13}C NMR(DMSO- d_6): $\delta = 63.1(2\text{C}); 68.8(2\text{C}); 70.7(2\text{C}); 73.0(6\text{C})$

Gas chromatography–mass spectroscopy analysis

Samples were analyzed as trimethylsilyl derivatives using the following procedure. In a screw-capped vial, a sample of ~ 1 mg of product was dissolved

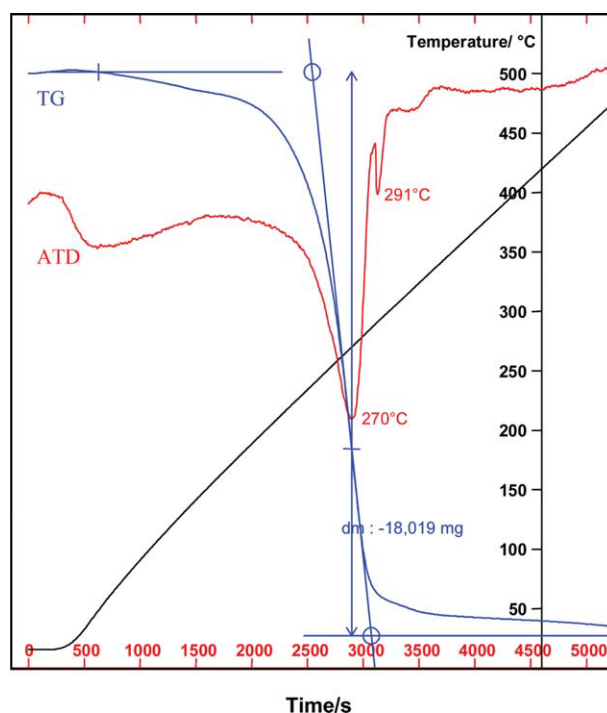


Figure 1 TG–DTA analysis of glycerol carbonate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in 0.5 mL of anhydrous acetonitrile (Acros Organics) and 0.4 mL of *N,O*-bis(trimethylsilyl) trifluoroacetamide containing 1% trimethylchlorosilane (Acros Organics) was added. The solution was sonicated for about 1 min and heated at 60°C for 20 min. After evaporation of the solvent in a stream of dry nitrogen, the residue was diluted in 1 mL of anhydrous ethyl acetate. Gas chromatography–mass spectroscopy (GC–MS) analysis was performed on a Clarus® 500 GC gas chromatograph (Perkin–Elmer, USA) coupled to a Clarus 500 MS quadrupole mass spectrometer (Perkin–Elmer). Gas chromatography was carried out on a 5% diphenyl/95% dimethyl polysiloxane fused-silica capillary column (DB-5 ms, 30 m \times 0.25 mm, 0.25-mm film thickness, J and W Scientific, USA). The gas chromatograph was equipped with an electronically controlled split/splitless injection port. The injection (1 μL) was performed at 250°C in the split mode (split flow of 40 mL/min). Helium was used as carrier gas, with a constant flow of 1 mL/min. The oven temperature program was as follows: 60°C constant for 2 min, 60–300°C at a rate of 10°C/min, and then constant for 9 min. Ionization was achieved under the electron impact mode (ionization energy of 70 eV). The source and transfer line temperature were 200°C. Detection was carried out in scan mode: m/z 50–700. The detector was switched off in the initial 2 min. Compounds were identified in comparison with

TABLE I
Microwave-Assisted Polymerization of Glycerol Carbonate (500 mg) Under Different Curing Conditions

Entry	Puissance (W)	Final weight (mg)	Time (min)	Temperature (°C)	Evolution of the IR band at 1780 cm ⁻¹
1 ^a	50	490	60	150	No evolution
2 ^a	100	480	60	180	No evolution
3 ^a	150	480	60	220	No evolution
4 ^a	160	450	60	240	Decrease
5 ^a	170	420	60	250	Decrease
6 ^a	180	400	60	260	Not observed
7 ^a	180	470	30	260	Decrease
8 ^a	200	370	50	280	Not observed
9 ^a	180	390	240	260	Not observed
10 ^b	200	380	30	280	Not observed

^a Reaction performed in a closed reactor.

^b Reaction performed in an open reactor.

authentic standards of linear oligomers with well-defined structures and degree of polymerization from two to four.

SEC analysis

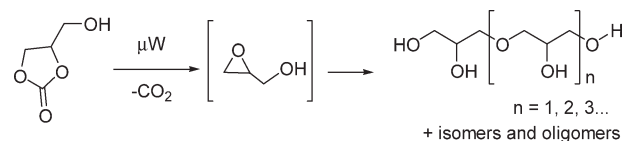
Relative molecular weights of oligomers were determined with respect to poly(ethylene glycol) standards by size exclusion chromatography (SEC). A Waters' associate system was used, equipped with a linear Waters Styragel HR1 column (maximal accuracy from 100 to 5000 g mol⁻¹), and a Waters 410 refractometer. All samples were analyzed at 40°C. Samples were dissolved in *N,N*-dimethylformamide (Acros Organics) at a concentration of 2.0 wt % and the injection volume was equal to 20 μL. *N,N*-dimethylformamide was used as eluent with a flow rate of 1.0 mL min⁻¹.

RESULTS AND DISCUSSION

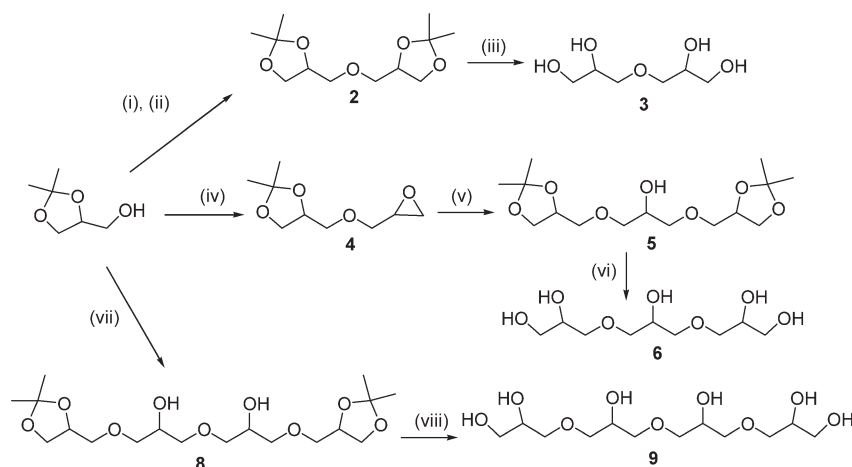
Polymerization of glycerol carbonate was initially investigated under classical thermal activation with or without catalysts. In all cases, reactivity of glycerol carbonate was checked by FTIR following the evolution of the carbonyl band at 1780 cm⁻¹ characteristic of the five-membered cyclic carbonate. Without catalyst, no reaction was observed up to 140°C, while higher temperatures lead to a partial decrease of the intensity of the band at 1780 cm⁻¹ due to hydrolysis of glycerol carbonate to glycerol by residual water present in the starting material. In the presence of catalytic amounts of bases such as sodium methoxide or potassium tert-butoxide (0.05 eq.), hydrolysis takes place at lower temperature leading to total hydrolysis of glycerol carbonate at 100°C. Formation of glycerol was confirmed by ¹H and ¹³C NMR spectroscopy, which indicates unambiguously formation of glycerol. Catalytic amounts of acids

such as *para*-toluenesulfonic acid, acetic acid, or zinc chloride have no effect on glycerol carbonate, which remained unchanged after heating at 100°C. Further experiments, using TG-DTA analysis, indicated an exothermic peak at 270°C corresponding to decarboxylation of glycerol carbonate, leading to the formation of glycidol, which was immediately vaporized without the formation of polyglycerol (Fig. 1).

Because of increasing interest for the use of microwave irradiation as a common heat source in polymer synthesis,¹⁸ reactivity was then investigated under microwave activation. Results are summarized in Table I. Contrary to the classical thermal activation, microwave irradiation resulted in a rapid disappearance of the characteristic FTIR carbonyl band of the cyclic carbonate. In the same time, any new carbonyl band can be detected indicating either formation of glycerol or polyglycerol. ¹H NMR analysis of the crude reaction mixture showed broad signals between 3 and 4 ppm similar to those observed for polyglycerol produced by Novance under alkaline etherification conditions indicating without any ambiguity decarboxylation and polymerization of glycerol carbonate (Scheme 1). Power of 180 W was necessary to initiate decarboxylation and polymerization of glycerol carbonate. Even if temperatures reached under microwave heating and TG-DTA analysis are quite similar, microwave activation allows polymerization of glycidol, while this latter one was vaporized under classical thermal-heating conditions. Reaction was also performed under



Scheme 1 Microwave-assisted polymerization of glycerol carbonate.



Scheme 2 Synthesis of reference linear di, tri, and tetraglycerols. Reagents: (i) NaH, DMF; (ii) *D,L*- α,β -isopropylidene-glycerol tosylate (**1**) (52%); (iii) Dowex 50WX8, MeOH, reflux (82%); (iv) aq. 50% NaOH, hexane, Bu₄NBr (cat.), 60°C (66%); (v) *D,L*- α,β -isopropylidene-glycerol, aq. 50% NaOH, hexane, Bu₄NBr (cat.), 60°C (47%); (vi) Dowex 50WX8, MeOH, reflux (45%); (vii) 1,2:6,7-diepoxy-4-oxaheptane (**7**), aq. 50% NaOH, hexane, Bu₄NBr (cat.), 60°C (42%); (viii) Dowex 50WX8, MeOH, reflux (75%).

microwave irradiation under similar conditions in an open vial to evaluate the influence of pressure on polymerization of glycidol (entry 10). Similar results were obtained, indicating decarboxylation and polymerization of formed glycidol. Irradiation of glycidol under the same experimental conditions leads to the formation of a product presenting similar NMR signals, while glycerol irradiated under the same conditions remains unchanged. Besides the advantages of fast and homogeneous heating allowed by the use of microwave activation, nonthermal microwave effects due to specific heating of polar intermediates should be involved to explain results obtained under microwaves. Indeed, similar observations have been reported by Chatti and coworkers during the synthesis of poly(ether-ester)s from aliphatic diol and acid chlorides under microwave irradiation.¹⁹ These authors observed an acceleration of the polymerization rate under microwave irradiation compared to the classical thermal heating under the same conditions, which was ascribed to the enhanced polarity of the transition state during the ester formation. Similarly, ring-opening polymerization of glycidol concerns neutral molecules in the ground state leading to charged species in the dipolar transition state. The formation of dipolar transition state, as the reaction is progressing, increases the sensitivity of the charged molecules to the electric field improving polymerization rate. This effect was also observed in several cases in the literature.^{20–26} In the same time, it seems that microwave heating is relatively similar to classical heating as concerns the temperature of decarboxylation of glycerol carbonate, which occurred around 270°C during TG analysis and for temperatures comprised between 240 and 280°C under microwave irradiation.

To have deeper insight on the polydispersity of the product, different linear oligomers (di, tri, and tetraglycerol) were synthesized (Scheme 2) and compared to oligomers present in polyglycerol mixtures obtained under microwave activation or classical thermal etherification conditions using SEC and GC-MS. Linear di, tri, and tetraglycerols were synthesized according to the known procedures.¹¹ Diglycerol was obtained by reaction of solketal (*D,L*- α,β -isopropylidene-glycerol) with its tosylate derivative followed by the removal of acetonide group,²⁷ while

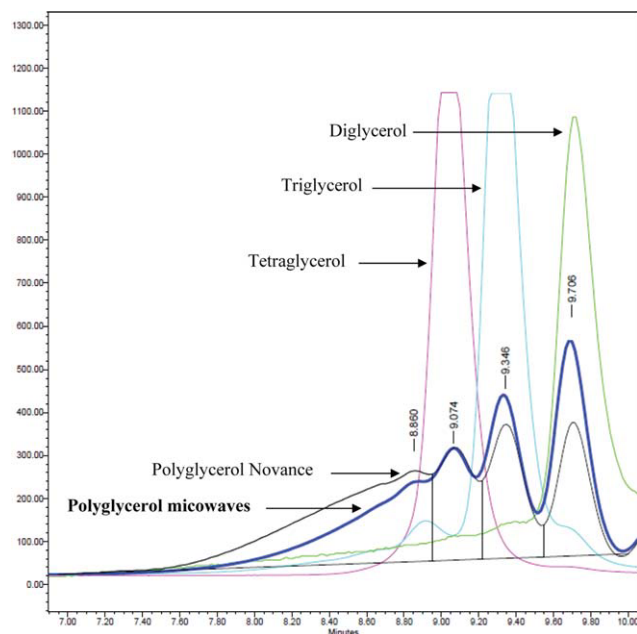


Figure 2 SEC chromatograms of glycerol oligomers obtained under different conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

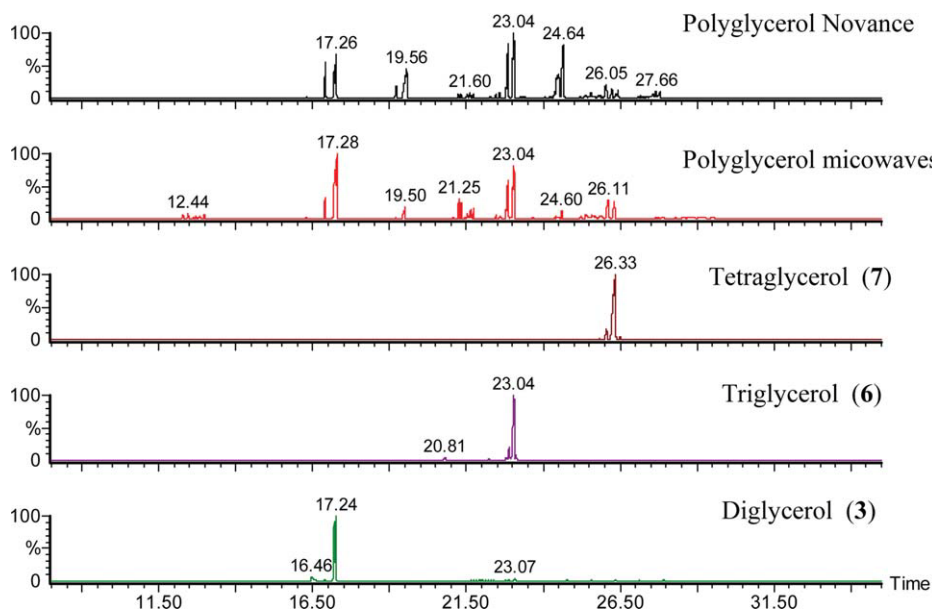


Figure 3 GC-MS chromatograms of glycerol oligomers obtained under different conditions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

triglycerol was obtained by reaction of solketal with glycidyl solketal ether followed by the removal of acetonide group.²⁸ Linear tetraglycerol was prepared from 1,2 : 6,7-diepoxy-4-oxaheptane, easily obtained by the oxidation of commercially available allyl 2,3-epoxypropyl ether, by the treatment of an excess of solketal in the presence of aqueous sodium hydroxide under phase-transfer conditions. Purification by column chromatography and subsequent acid-catalyzed hydrolysis of bis(dioxolane) gave the expected, unprotected linear tetraglycerol.¹¹

Size exclusion chromatograms of reference polyglycerol furnished by Novance and of polyglycerol synthesized under microwaves are presented in Figure 2. Even if small differences can be detected, overall aspect of both chromatograms is quite similar. Both products contained mainly low-molecular weights oligomers corresponding to diglycerol at 9.70 min, triglycerol at 9.34 min, tetraglycerol at 9.07 min, and more or less important quantities of higher molecular weights oligomers. Polymerization carried out under microwave activation leads to oligomers of slightly lower molecular weights compared to polyglycerol obtained by polyetherification carried out under alkaline conditions by Novance. This behavior could be explained by the difference of mechanisms under both conditions. Indeed, microwave-assisted polymerization involves decarboxylation of glycerol carbonate leading to formation of glycidol, which reacts with hydroxyl groups leads to the formation of ether bond without further possibility of reaction, whereas polyetherification of glycerol under alkaline conditions leads in theory to higher DP according to the quantity of water removed from

the reaction mixture. GC-MS chromatograms of both polyglycerols and of reference di, tri, and tetraglycerols are presented in Figure 3. Similarly, to results obtained by SEC, GC analysis indicated the presence of di, tri, and tetraglycerols. In addition to linear oligomers, ramified or cyclic oligomers can be detected in both polyglycerols mixtures. Polyglycerol, synthesized under alkaline condition, contains higher quantity high-molecular weight oligomers comparatively to polyglycerol obtained under microwaves. Amounts of other ramified or cyclic oligomers differ slightly according to the origin of polyglycerol. Molecular peaks of each glycerol oligomer were not detected probably due to the instability of these latter ones under analytical conditions used.

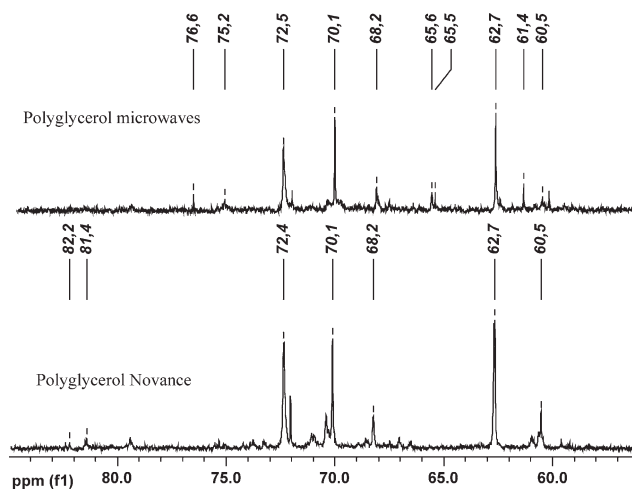
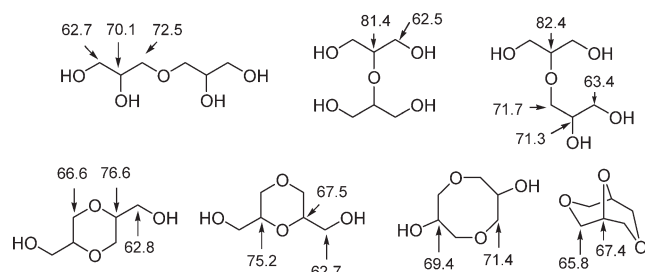


Figure 4 ¹³C NMR spectra of glycerol oligomers obtained under different conditions.



Scheme 3 Predicted chemical shifts of the different cyclic and acyclic diglycerol oligomers using NMR predictor software.

Further analyses were carried out by ^{13}C NMR to investigate the nature of the different isomers present in both mixtures (Fig. 4). According to literature data¹¹ and to calculated values obtained by simulation with C NMR Predictor ACD/Labs 8.09 software (ACD, Ontario, Canada), the main signals at 62.7, 70.1, and 72.5 ppm were attributed to the different carbon atoms of linear oligomers, similar to those observed in reference compounds (Scheme 3). Presence of ramified oligomers can be detected by the signals at 81.4 and 82.2 ppm characteristic of prim-sec and sec-sec linkages present in oligomers,¹¹ while signals at 75.2 and 76.6 ppm were characteristic of cyclic structures.

CONCLUSIONS

According to all these results, glycerol carbonate appears as a valuable starting material for the synthesis of glycerol oligomers under relatively mild conditions using microwave activation. Under these conditions, reaction can be carried out without the use of any solvent or reactant and for relatively short-reaction times. Even if classic alkaline polymerization procedure starting directly from glycerol seems a more efficient procedure presenting higher atom economy, microwave-assisted polymerization of glycerol carbonate present the advantages to use less-hazardous conditions, better energy efficiency, and safer solvent and auxiliaries due to the experimental conditions used without involving any solvent, reactant, or purification procedure. In both cases, polymerization processes produce low-molecular weight oligomers with relatively similar composition even if small differences have been observed. Moreover, glycerol carbonate, easily synthesized using an environmental friendly inexpensive process from glycerol and urea, can be considered as a safe and renewable starting material. Compared to classical thermal heating, microwave irradiation presents the advantage of a fast and homogeneous heating

allowing high-temperature chemistry, but also non-thermal microwave effects due to specific heating of polar intermediates produced during reaction leading to modified selectivity enabling polymerization that cannot be performed with thermal heating.

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