



# Free radical polymerization study of glycerin carbonate methacrylate for the synthesis of cyclic carbonate functionalized polymers

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## ABSTRACT

This article describes for the first time a complete study of the free radical polymerization (FRP) of (2-oxo-1,3-dioxolan-4-yl) methyl methacrylate or glycerin carbonate methacrylate (**GCMA**). This methacrylic cyclic carbonate compound allows the synthesis of polymers bearing cyclic carbonate functional groups which can be used for crosslinking reactions in other to form urethane linkages without the use of harmful isocyanates. Transfer reactions to the cyclic carbonate moiety were identified during the polymerization of **GCMA**. Moreover, a transfer constant of 0.011 was obtained when a cyclic carbonate compound, the acetate of glycerin carbonate is used as transfer agent during the polymerization of MMA. A calculation of the  $k_p^2/k_t$  value of **GCMA** in DMSO proves the high reactivity of this monomer since the value obtained ( $245 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ) is almost 2 times higher than methyl methacrylate (MMA) value ( $149 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ) in the same conditions. Glass transition temperatures of homopolymers of **GCMA** (114 and 134 °C) were measured for the first time. Finally the calculation of the reactivity ratios  $r_{\text{MMA}}$  (0.5) and  $r_{\text{GCMA}}$  (2.0) during the copolymerization of **GCMA** with MMA in DMSO, by the Macret's method shows again the high reactivity of this monomer.

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## 1. Introduction

Improvement in the thermal, mechanical, surface or physicochemical properties of polymers is an important challenge in polymer chemistry. In the current economic and environmental context, modification and improvement of already known polymers are preferred rather than the synthesis of polymers from new monomers. Cross-linking is thus the main method to improve properties starting from known and low molecular mass polymers [1]. Indeed it is a method of choice not only in order to improve the properties of the polymers but also to reach high molar masses starting from oligomers or prepolymers or also in

order to increase the glass transition temperature of materials. Cross-linking systems are extensively used for coatings since they allow a two-step synthesis, appreciated in industry: first the formulation and then the cross-linking on the substrate. Due to their cross-linking ability, polymers bearing reactive functionalities and curing agents have large potential for coatings and other related applications. Indeed, systems such as phenol-formol [2] or epoxy-amine [3] are widely used to cross-link polyacrylates. However the toxicity of compounds such as formaldehyde or glycidyl methacrylate, which is used as epoxy cross-linker, raises problems and all these compounds are increasingly controlled by the current regulations and should be replaced. Polyacrylates are also extensively used in urethane systems [4]. 2-Hydroxyethyl acrylate is a monomer of choice for the introduction of hydroxyl reactive

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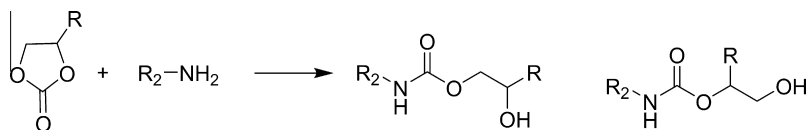


Fig. 1. Aminolysis reaction of cyclic carbonate with amine.

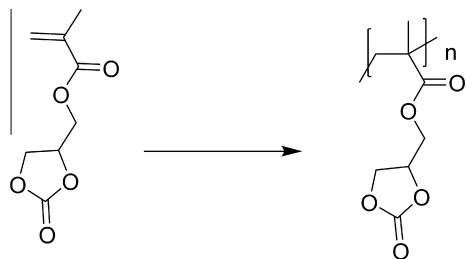


Fig. 2. Polymerization of (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate (GCMA).

functionalities in polyacrylates. The cross-linking is carried out by adding a diisocyanate in formulation, reacting on hydroxyl functions and leading to carbamate linkages, responsible for the good properties of such kinds of coatings. The main drawback of this chemistry is also the use of isocyanates which are very harmful reactants. In order to overcome this issue, the synthesis of non-isocyanate polyurethanes has recently gained a great interest in chemical industry: step growth polymerization of dicyclo-carbonates and diamines can be an alternative route for the synthesis of conventional polyurethanes (Pus) without the use of isocyanates [5–12].

Interestingly, cyclic carbonates present in a polymer chain as pendant functional groups, could react with amines conducting in the formation of hydroxyl-urethane linkages with primary and secondary hydroxyl units (Fig. 1).

This kind of system can be used as a cross-linking system to obtain urethane linkages without the use of toxic isocyanates. Moreover, the presence of hydroxyl functions leads to supplementary hydrogen bonds which give advantages to polyhydroxyurethanes (PHUs) over conventional polyurethanes, with for example a lower porosity [13]. PHUs also exhibit higher chemical stability, since no thermally unstable biuret and allophanate units are formed, which usually go along with the reactions between diisocyanate and diols. Taking into account of this approach, homopolymers and copolymers bearing cyclic carbonate functional groups have been reported by various researchers [14–33].

The introduction of cyclic carbonate moieties by polymerization of cyclic carbonate monomers is an interesting possibility to obtain a functionalized polymer. Thus, scientists are paying increasing interest to monomers bearing reactive cyclic carbonate groups. We previously reported the synthesis and the applications of unsaturated cyclic carbonate compounds [34] which have two different reactive groups: the first one intended to polymerize or to copolymerize with other comonomers and the second

one for crosslinking reactions. (2-Oxo-1,3-dioxolan-4-yl)methyl methacrylate or glycerine carbonate methacrylate (GCMA) (Fig. 2) is the most studied monomer for the synthesis of carbonate functionalized polymers.

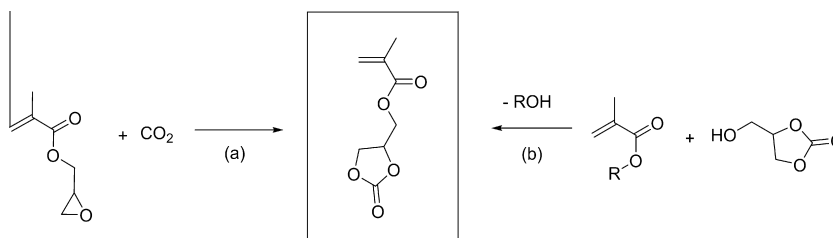
This monomer is currently commercialized by few companies such as Specific Polymers [35]. In the literature, several synthetic routes based on the synthesis of the carbonate moiety and the grafting of the methacrylic functionality were reported [17,26,36–48]. Among all these routes, the most interesting ones to obtain GCMA remain the carbonation of glycidyl methacrylate (Fig. 3, route (a)) and the transesterification of alkyl methacrylate such as methyl methacrylate with glycerin carbonate (Fig. 3, route (b)). Indeed carbonation is the most quantitative way to obtain pure cyclic carbonate and concerning the transesterification route, the use of methyl methacrylate which is cheap and easily available commercially and the use of glycerin carbonate which is partially biosourced are advantages.

Although some researchers studied the radical polymerization of GCMA [38,49,50]; according to its high reactivity, its polymerization was never entirely described. In order to allow the synthesis of polymer bearing carbonate moieties, particularly at the industrial scale, it is crucial to perform the complete study of the free radical polymerization of GCMA. So, herein we studied and compared the two most interesting methods (a and b) for the synthesis of GCMA, we studied the polymerization and the copolymerization of this monomer, and we also focused on the kinetics of polymerization. First, commercially available GCMA obtained both by carbonation and transesterification was copolymerized with some usual acrylic, methacrylic and styrenic monomers in order to study the influence of the synthesis method on radical polymerization. Then GCMA was homopolymerized by conventional radical polymerization in DMSO and compared to the carbonated homopolymer polyGMA. The high reactivity of GCMA was proven by the calculation of the characteristic constant of polymerizability ( $(k_p^2/k_t)$ ) where  $k_p$  is the propagation constant and  $k_t$  is the termination constant). And finally, the determination of reactivity ratios of GCMA and methyl methacrylate (MMA) during their copolymerization was also carried out. To the best of our knowledge, this is the first comprehensive study on copolymerization of GCMA by free radical polymerization.

## 2. Experimental

### 2.1. Materials and methods

The two samples of glycerin carbonate methacrylate synthesized by carbonation and by transesterification



**Fig. 3.** Synthesis routes to obtain (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate: (a) carbonation of glycidyl methacrylate, (b) transesterification of alkyl methacrylate.

(respectively **GCMAC** and **GCMAT**) [RNCAS 13818-44-5] were supplied by **Specific Polymers (France)** under the **reference SP 40-001**. Glycidyl methacrylate (97%) (GMA), *n*-butyl acrylate (99%) (nBA), styrene (99%) (Sty), methyl methacrylate (99%) (MMA), methacrylic acid (99%), acetic anhydride (99%), 4-(Hydroxymethyl)-1,3-dioxolan-2-one (glycerol carbonate) and 2-hydroxy ethyl acrylate (96%) (HEA) were supplied by Sigma Aldrich and used after distillation. Lithium bromide (LiBr) was supplied by Sigma Aldrich and used as received. Azobisisobutyronitrile (AIBN) was supplied by Sigma Aldrich and used after recrystallization. Other reagents such as pyridine, triphenylphosphine, dimethyl sulfoxide (DMSO), methyl ethyl ketone (MEK), acetonitrile, dichloromethane (DCM), *N,N*-dimethylformamide (DMF), methanol, toluene, were reagent grade and were used as received without further purification. Deuterated solvents ( $\text{CDCl}_3$  and  $\text{DMSO-d}_6$ ) were supplied by Eurisotop (Saint-Aubin, France).

IR spectra were recorded on a Nicolet 210 FT-IR spectrometer. The characteristic IR absorptions mentioned in the text were strong bands and are reported in  $\text{cm}^{-1}$ .

All Nuclear magnetic resonance ( $^1\text{H}$  NMR) measurements were recorded on a Bruker AC-400 MHz spectrometer at room temperature in deuterated chloroform ( $\text{CDCl}_3$ ) or dimethylsulfoxide ( $\text{DMSO-d}_6$ ). The chemical shifts were reported in parts per million relative to tetramethylsilane (TMS).

The molar masses of polymers were determined by steric exclusion chromatography or size exclusion chromatography. Size exclusion chromatography (SEC) was performed on a Varian ProStar Model 210 equipped with an RI refractive index detector. Two Polargel 5  $\mu\text{m}$  MIXED-C 600 mm were used at 70  $^\circ\text{C}$  with a 0.8  $\text{mL min}^{-1}$  flow rate of DMF, calibrated using PMMA standards.

Differential Scanning Calorimetry (DSC) measurements were performed with a calorimetric NETZSCH DSC 200 F3 calibrated with an indium standard. Samples of  $10 \pm 2$  mg were placed in the measurement heating cell. An empty pan was used as reference. All the samples were heated under inert atmosphere from  $-20$  to  $250$   $^\circ\text{C}$  at a heating rate of  $20$   $^\circ\text{C/min}$ . Three runs were recorded and the glass transition temperature ( $T_g$ ) values were measured during the second run and confirmed by a third run.

## 2.2. Synthesis of glycerine dimethacrylate

Glycerin dimethacrylate was synthesized as follow, in a round-bottom flask (25 mL), glycidyl methacrylate (2 g, 14 mmol) reacted with methacrylic acid (1.21 g, 14 mmol)

in the presence of triphenylphosphine (0.039 g, 0.14 mmol) at 50  $^\circ\text{C}$  during 16 h. The product was characterized without further purification by NMR analysis.

## 2.3. Homopolymers and copolymers of GCMA synthesis

Homopolymerization of **GCMA** (5 mmol) in DMSO (5 mL) was performed at 60  $^\circ\text{C}$  for 16 h under a nitrogen atmosphere. AIBN (3% (molar ratio)) was used as initiator. After polymerization the polymer was precipitated twice in methanol and dried under vacuum at 50  $^\circ\text{C}$  for 16 h. The same procedure was used for all the homopolymerization of **GCMA** in the other solvents.

Copolymerization of GCMA with comonomers (MMA, Abu and Sty) was performed in MEK (0.2 or 0.4 g/mL) at 70  $^\circ\text{C}$  for 16 h under a nitrogen atmosphere with AIBN (3% (molar ratio)) as initiator. After each polymerization the polymer was precipitated twice in methanol and dried under vacuum at 50  $^\circ\text{C}$  for 16 h.

## 2.4. Carbonation reaction

Carbonation reaction of the homopolymer of glycidyl methacrylate (GMA) was performed as follows: in an autoclave (500 mL), epoxide polymer and lithium bromide (LiBr, 5% (molar ratio)) were dissolved in dimethylformamide (DMF, enough to fill  $\frac{3}{4}$  of the autoclave). Then carbon dioxide was added (15 bars) and the reaction proceeded at 80  $^\circ\text{C}$  during 48 h. A quantitative conversion was observed by  $^1\text{H}$  NMR. Then, the polymer was precipitated twice in methanol and dried under vacuum at 50  $^\circ\text{C}$  for 16 h.

## 2.5. Synthesis of 4-[(acetyloxy)methyl]-1,3-dioxolan-2-one

For the synthesis of 4-[(acetyloxy)methyl]-1,3-dioxolan-2-one, glycerin carbonate (2 g, 16.95 mmol) reacted with acetic anhydride (1.9 g, 18.64 mmol, 1.1 eq) in dichloromethane (20 mL) and pyridine (1.47 g, 18.64 mmol) at room temperature during 16 h. After reaction, the mixture was washed with water, dried with anhydrous  $\text{MgSO}_4$ . And finally, dichloromethane was removed using a rotary evaporator.

## 2.6. Polymerization of MMA

MMA was polymerized in toluene (1 M) with AIBN (3% (molar ratio)) at 70  $^\circ\text{C}$  during 16 h. Various amount of glycerin carbonate acetate from 0 to 50 mol% with respect to

MMA concentration were added to the monomer before polymerization. After polymerization, polymers were precipitated twice in methanol and dried under vacuum at 50 °C for 16 h.

### 2.7. Determination of the $k_p^2/k_t$ ratio

Homopolymerization of **GCMA** (5 mmol) in DMSO (5 mL) was performed at 60 °C for 16 h under a nitrogen atmosphere. AIBN (10 mg, 1% (molar ratio)) was used as initiator. Nine samplings were performed at the beginning of the reaction during 90 min and these samples were analyzed by  $^1\text{H}$  NMR in order to determine the **GCMA** conversion. After polymerization, the polymer was precipitated twice in methanol and dried under vacuum at 50 °C for 16 h. Radical homopolymerizations of HEA, MMA and GMA in DMSO for the determination of  $k_p^2/k_t$  ratio were performed by the same way.

### 2.8. Calculation of GCMA and MMA reactivity ratio

Copolymerizations of **GCMA** with MMA were carried out in DMSO (1 M) at 60 °C with 1 mol% of AIBN. Samplings were performed at the beginning of the reaction and samples were analyzed by  $^1\text{H}$  NMR in order to determine GCMA and MMA conversion. After polymerization, poly-

mers were precipitated twice in methanol and dried under vacuum at 50 °C for 16 h.

## 3. Results and discussion

### 3.1. Monomers characterization

Before studying the radical polymerization of the monomer, **GCMA** obtained both by carbonation (**GCMAC**) and by transesterification (**GCMAT**) were characterized and studied. These two methods of synthesis were chosen since they are the most interesting synthesis methods at industrial scale. The aim of this study is to determine whether the synthesis method have an influence on the monomer and on its polymerization at an industrial scale. Therefore, for this study, **GCMAC** and **GCMAT** supplied by **Specific Polymers** were used without further purification, which is the case at industrial scale.

**GCMAC** was easily synthesized by the reaction of GMA with carbon dioxide. The conversion of the epoxide ring of GMA to the five-membered cyclic carbonate was total since the epoxide signals of GMA at 2.60, 2.80 and 3.20 ppm (Supporting Information Fig. S1) were replaced by the characteristic cyclic carbonate signals at approximately 4.40 and 4.80 ppm (Fig. 4 (up)). Concerning **GCMAT**

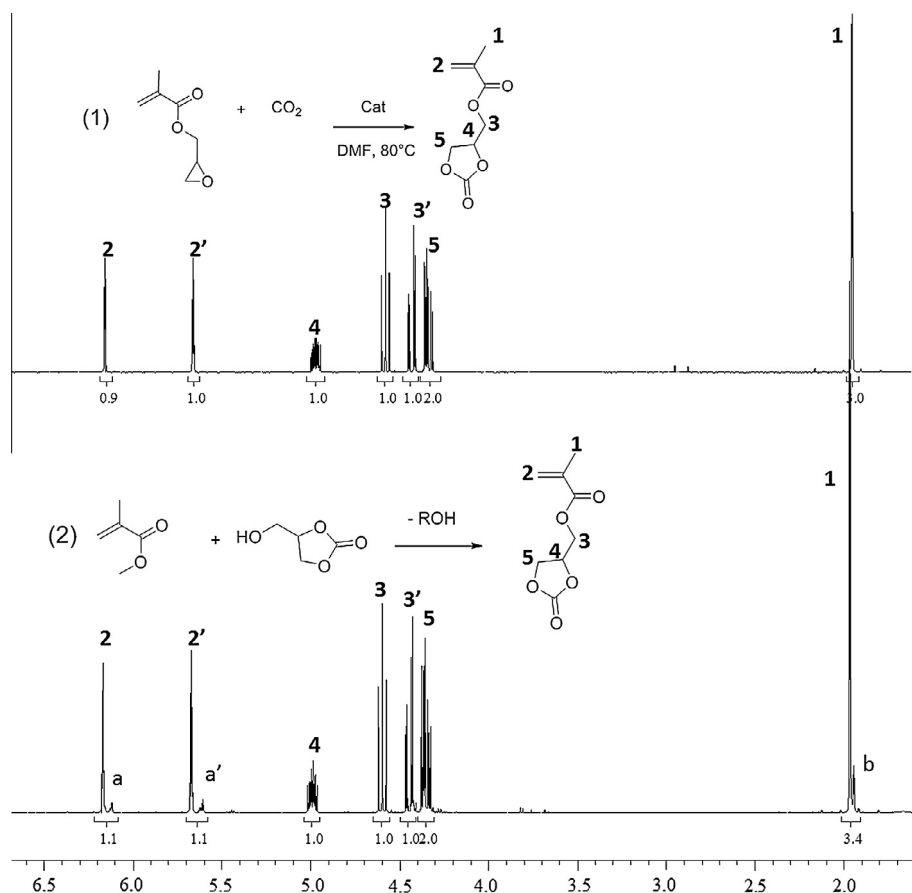


Fig. 4.  $^1\text{H}$ -NMR spectrum of **GCMA**: (1) synthesized by carbonation route, (2) synthesized by transesterification route.

obtained by transesterification between methacrylic acid and glycerin carbonate, the presence of the additional signals a and a' to 2 and 2' protons at 5.6 and 6.1 ppm and b to the proton 1 on the NMR spectrum displays a lower purity than **GCMAC** and shows the presence of additional methacrylic moieties (Fig. 4 (down)).

In order to further characterize this monomer, **GCMAT** was also characterized by  $^{13}\text{C}$  NMR (Supporting Information Fig. S2 (down)), this analysis pointed out the presence of other methacrylic functions as previously observed on  $^1\text{H}$  NMR spectrum. Indeed glycerin carbonate used for the synthesis of **GCMA** by transesterification reaction contains a low amount of glycerin and other unidentified carbonates [51] which can react with MMA to yield different methacrylic compounds. Among all these additional compounds, the two isomers of glycerin dimethacrylate can be formed by the reaction of glycerin with MMA (Fig. 5 (1), a and a'). In order to confirm the presence of glycerin dimethacrylate in the supplied **GCMAT**, we performed the synthesis of this compound by the reaction between methacrylic acid and glycidyl methacrylate with triphenylphosphine at 50 °C according to the following equation (Fig. 5 (2)).

The comparison of both  $^{13}\text{C}$  NMR analysis of the synthesized dimethacrylate and **GCMAT** confirms that the residual peaks in **GCMAT** correspond to the presence of glycerin dimethacrylate (Supporting Information Fig. S2).

The quantity of glycerin dimethacrylate in **GCMAT** is equal to 10%, this value was easily estimated by  $^1\text{H}$  NMR analysis (see Fig. S3 in Supporting information). Such dimethacrylate is not observed in **GCMAC** obtained by the carbonation method since pure GMA is used for this synthesis.

The presence of such difunctional monomer in **GCMAT** can cause trouble during the polymerization according to its cross-linking ability. Therefore the copolymerization study of the two different **GCMA** was performed in order to evaluate the influence of glycerin dimethacrylate on the polymer synthesis.

### 3.2. Copolymerization reaction of GCMA with various acrylic, methacrylic and styrenic monomers

Both **GCMA** obtained by carbonation (**GCMAC**) and by transesterification (**GCMAT**) were copolymerized with

styrene (Sty), butyl acrylate (ABu) and methyl methacrylate (MMA). These three comonomers were chosen due to their extensive use in the synthesis of vinyl and acrylic polymers for coating applications. Indeed, methyl methacrylate gives supplementary exterior durability, hardness and water resistance, whereas styrene is used for cost reduction and also to improve the hardness of the film formulated. Concerning butyl acrylate, it is principally used in order to add flexibility and water resistance to the formulation [52]. Thus, the combination of these monomers which yield very different glass transition temperatures ( $T_g$ ), could allow to modulate the  $T_g$  of the synthesized copolymer.

The aim of this copolymerization study was to compare both **GCMA** in order to determine the influence of the presence of glycerin dimethacrylate on the polymerization and then to determine the best synthesis route. For each monomer, polymerizations were carried out with AIBN as initiator in methyl ethyl ketone at 70 °C during 16 h. The polymers were first analyzed by  $^1\text{H}$  NMR analysis in order to determine the monomer conversions and the polymer compositions. The polymers were also characterized after purification by size exclusion chromatography. The results of these polymerizations are summarized in Table 1.

These results show that for both monomers, copolymerization always occurred with relatively good conversion. However in the case of the copolymers with **GCMAT**, monomer conversions were lower than for copolymers with **GCMAC**, while terpolymers with both **GCMAC** and **GCMAT** exhibited similar monomer conversions. The monomer purity affects the copolymerization of **GCMA** but has no effect on the conversion, when more than two different monomers were used. The fact that polymer compositions were close to the monomer feeds for all the polymerizations, means that **GCMA** can easily polymerize with the acrylic, methacrylic and styrenic monomers used.

However, PDI are higher for polymers obtained with **GCMAT** (10.8, 2.9 and 10.2) than for polymers with **GCMAC** (1.7). This increase of PDI with **GCMAT** is due to the presence of the dimethacrylate previously identified, which can entail polymer cross-linking, and broadening of polymer masses even at low concentration. To conclude, all these results prove that the presence of glycerin dimethacrylate in **GCMAT** can disturb the polymerization and thus this method of production of GCMA should not be the

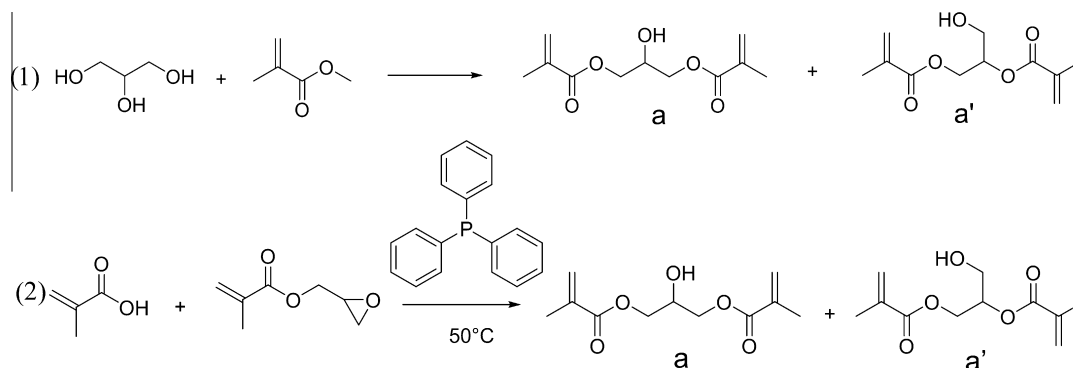


Fig. 5. Synthesis of both isomers of glycerine dimethacrylate, (1) starting from glycerin and (2) starting from methacrylic acid and glycidyl methacrylate.

**Table 1**  
Copolymerization of **GCMAC** and **GCMAT** under conventional radical polymerization.

Run	Monomer feed (wt%)				Monomer conversion (wt%)				Polymer composition (wt%)				SEC characterization	
	GCMAC	MMA	Sty	nBA	GCMAC	MMA	Sty	nBA	GCMAC	MMA	Sty	nBA	Mn <sup>c</sup>	Mw/Mn
1 <sup>a</sup>	30	70	–	–	96	97	–	–	29	71	–	–	12,600	1.7
2 <sup>b</sup>	20	40	40	–	89	52	74	–	29	22	49	–	10,200	1.7
3 <sup>b</sup>	20	40	–	40	99	97	–	96	21	40	–	39	23,600	1.7
Run	GCMAT	MMA	Sty	nBA	GCMAT	MMA	Sty	nBA	GCMAT	MMA	Sty	nBA	Mn <sup>c</sup>	Mw/Mn
4	30	70	–	–	88	86	–	–	28	72	–	–	12,700	10.8
5 <sup>b</sup>	20	40	40	–	89	52	53	–	28	36	36	–	17,900	2.9
6 <sup>b</sup>	20	40	–	40	99	99	–	92	21	41	–	38	39,700	10.2

<sup>a</sup> Reaction was carried out at 0.2 g/mL concentration of monomers in MEK at 70 °C for 16 h.

<sup>b</sup> Reactions were carried out at 0.4 g/mL concentration of monomers in MEK at 70 °C for 16 h.

<sup>c</sup> Calculated from <sup>1</sup>H NMR.

avored one. Therefore, for the rest of our work **GCMAC** is the most appropriate monomer to study.

### 3.3. Direct homopolymerization versus carbonation

In order to study the radical polymerization of GCMA, the homopolymerization of this monomer was first carried out. Radical polymerization of GCMA was studied under several conditions. Two parameters were studied: the influence of the solvent used for the polymerization and the influence of the GCMA concentration. The results are summarized in [Tables 2 and 3](#). All the polymerizations were performed at 60 °C for 16 h with AIBN as initiator.

GCMA homopolymerizes very well since the monomer conversions were close to 99% for all polymerizations but some cases of gelation were noticed. As observed by Endo [\[49\]](#) in their study of GCMA polymerization, bulk polymer-

ization leads to gelation. In acetonitrile and toluene, the polymer which precipitates during polymerization is only soluble in DMSO or DMF. In methyl ethyl ketone, the polymerization of GCMA leads to gelation after 16 h. Dimethyl sulfoxide, which is a polar aprotic solvent, seems to be an appropriate solvent for the polymer since it solubilizes the homopolymer and allows the synthesis of a polymer with a high molar mass and a low PDI. The influence of the GCMA concentration in DMSO was also studied ([Table 3](#)), the obtained SEC traces for the polymers obtained in DMSO are reported in [Supporting information](#) (see [Fig. S4 in Supporting information](#)).

Polymerization in DMSO occurs without any precipitation or gelation up to a concentration of 2.4 mol L<sup>-1</sup> and a gelation is observed for a monomer concentration of 3 mol L<sup>-1</sup>. These results can be explained by a possible chain transfer reaction to the cyclic carbonate moieties

**Table 2**  
Radical polymerization of **GCMA** in various solvents.

Run <sup>a</sup>	[GCMAC] (mol L <sup>-1</sup> )	Solvent	Monomer conversion (%) <sup>c</sup>	Mn <sup>d</sup> (g mol <sup>-1</sup> )	Mw/Mn <sup>d</sup>
1	Bulk	–	Gelation	–	–
2	1.2	Toluene	97 <sup>b</sup>	63,000	4.1
3	1.2	MEK	Gelation	–	–
4	1.2	Acetonitrile	97 <sup>b</sup>	14,000	1.5
6	1.2	DMSO	99	86,000	2.4

<sup>a</sup> 3% (molar ratio) of AIBN for 16 h at 60 °C.

<sup>b</sup> Polymer precipitation during polymerization.

<sup>c</sup> Determined from <sup>1</sup>H NMR.

<sup>d</sup> Estimated from size exclusion chromatography.

**Table 3**  
Radical polymerization of **GCMA** in DMSO.

Run <sup>a</sup>	[GCMAC] (mol L <sup>-1</sup> )	Monomer conversion (%) <sup>b</sup>	Mn <sup>c</sup> (g mol <sup>-1</sup> )	Mw/Mn <sup>c</sup>
5	0.6	99	62,000	2
6	1.2	99	86,000	2.4
7	1.8	99	90,000	2.6
8	2.4	99	102,000	2.9
9	3.0	Gelation	–	–

<sup>a</sup> 3% (molar ratio) of AIBN for 16 h at 60 °C.

<sup>b</sup> Determined from <sup>1</sup>H NMR.

<sup>c</sup> Estimated from size exclusion chromatography.



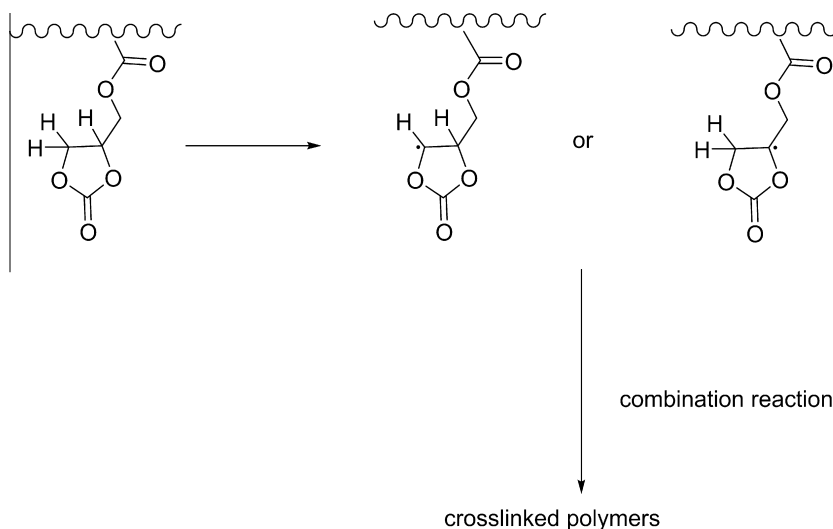


Fig. 6. Transfer reactions to polymer of GCMA.

by abstraction of the hydrogen attached to the carbonate group and combination of the radicals resulting in a cross-linked polymer (Fig. 6).

This possibility of cross-linking was first proposed by Brosse [53] with the acrylate bearing cyclic carbonate and a few years later by Endo [49] who confirmed this transfer reaction by performing the radical polymerization of MMA initiated by benzoyl peroxide (BPO) in propylene carbonate (0.2 M) at 100 °C. After polymerization, the incorporation of the propylene carbonate moiety into PMMA was first put in relief by IR. The IR spectrum of the poly(methyl methacrylate) obtained showed an absorption band at 1809  $\text{cm}^{-1}$  corresponding to the 5-membered cyclic carbonate. Moreover,  $M_n$  was estimated to 7800 g/mol which is smaller than expected for the radical polymerization of MMA in such conditions.

Although Endo has observed qualitatively this transfer reaction to cyclic carbonate moieties, in this paper we performed a further study of this eventuality. First, we performed the synthesis of the acetal of glycerin carbonate 4-[(acetyloxy)methyl]-1,3-dioxolan-2-one, according to Fig. 7.

Then increasing amounts of this compound were added during the polymerization of MMA in order to evaluate the effect of cyclic carbonate group, as transfer agent. MMA was polymerized in toluene (1 M) with AIBN (3%) at 70 °C during 18 h. Various amounts of glycerin carbonate acetate from 0% to 50% (molar ratio) with respect to

MMA concentration were added to the monomer before polymerization and the molar masses of the polymers obtained were measured by SEC (Table 4).

Fig. S5 (in Supporting information) shows that molar masses of PMMA decrease when the amounts of glycerin carbonate acetate increase. These results prove that the carbonate compound could be used as an efficient transfer agent. Then we performed for the first time the calculation of a transfer constant during such polymerization in order to quantify the transfer effect of this cyclic carbonate compound.

We used the method established in our lab by Bauduin et al. [54] to determine the transfer constant of some thiols with methacrylic monomers. In this previous study, theoretical instantaneous polymerization degree  $(DP_n)_i$  can be determined from Eq. (1), which is a version of the Mayo Eq. (2) adapted to radical chain transfer polymerization.

$[X]$  represents the chain transfer agent (CTA) concentration and  $[M]$  the monomer concentration.

$$\frac{1}{(DP_n)_i} = C_T R_0 \quad (1)$$

$$\frac{1}{(DP_n)_i} = \frac{1}{(DP_n)_0} + C_T \frac{[X]}{[M]} \quad (2)$$

With  $R_0 = \frac{[X]}{[M]}$  and  $C_T = \frac{k_{tr}}{k_p}$ , the transfer constant of the CTA.

The method used is based on the measurement of the polymerization degrees, real  $(DP_n)$  or cumulated  $(DP_n)_{cum}$  for a given rate of conversion  $\alpha_M$  according to the Eq. (3).

$$(DP_n)_{cum} = \frac{\alpha_M}{R_0 [1 - (1 - \alpha_M)^{C_T}]} \quad (3)$$

This equation can also be written as follow: (Eq. (4))

$$\log \left( 1 - \frac{\alpha_M}{R_0 (DP_n)_{cum}} \right) = C_T \cdot \log(1 - \alpha_M) \quad (4)$$

The graphical representation of  $\log \left( \frac{\alpha_M}{R_0 [1 - (1 - \alpha_M)^{C_T}]} \right) = f(\log(1 - \alpha_M))$  is a straight line. The slope of the line corresponds to  $C_T$ .

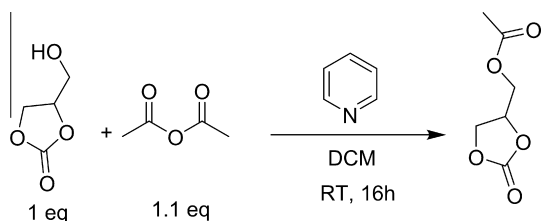


Fig. 7. Synthesis of 4-[(acetyloxy)methyl]-1,3-dioxolan-2-one.

**Table 4**

Effect of glycerin carbonate acetate 4-[(acetyloxy)methyl]-1,3-dioxolan-2-one in the radical polymerization of MMA in Toluene.

Run <sup>a</sup>	[glycerin carbonate acetate] <sub>0</sub> /[MMA] <sub>0</sub> (%)	Mn <sup>b</sup> (g mol <sup>-1</sup> )	Mw/Mn <sup>b</sup>
1	0	17,300	1.5
2	5	16,000	1.5
3	10	15,900	1.5
4	20	15,870	1.4
5	40	12,500	1.4
6	50	11,900	1.3

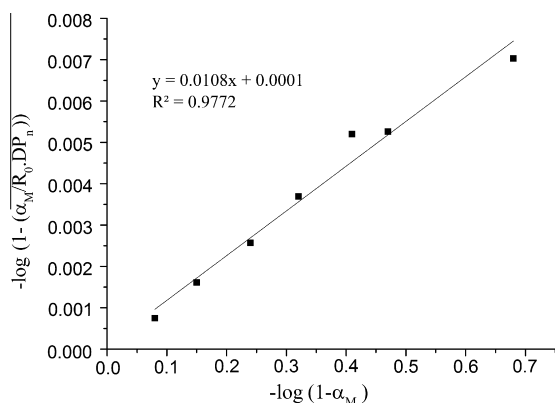
<sup>a</sup> 3% (molar ratio) of AIBN for 16 h at 70 °C in toluene (1 M).

<sup>b</sup> Estimated from size exclusion chromatography (eluent: DMF, calibration based on PMMA).

For this calculation, sampling was carried out during the polymerization of MMA in the presence of 40 mol% of glycerin carbonate acetate with respect to MMA concentration. For each sample  $DP_{cum}$  is determined by SEC and  $\alpha_M$  by <sup>1</sup>H NMR.

Fig. 8 shows the line obtained for this experiment with a slope of 0.011 corresponding to the transfer constant of the cyclic carbonate compound. This value is not negligible compared to the transfer constants of some usual and very efficient CTA such as ethanethiol and 2-mercaptoethanol with transfer constant values respectively of 0.1549 and 0.4049 at the same temperature [56].

Therefore, chain transfer reactions to the cyclic carbonate moieties and combination of the formed radicals resulting in a crosslinking are confirmed by our study. Although transfer constant of **GCMA** should be different from that of acetate of glycerin carbonate this study proves that cyclic carbonate compounds can be responsible for the occurrence of transfer reactions. It would be possible to get the transfer constant of **GCMA** directly but this determination would be more difficult and therefore also inaccurate. Transfer reactions to the cyclic carbonate increasing with the carbonate concentration, **GCMA** concentration must be as low as possible during the polymerization. Indeed, when **GCMA** concentration increases, molar masses increase, with the formation of a partially cross-linked polymer. Taking into account the occurrence of such kind of transfer reactions during **GCMA** homopolymerization,



**Fig. 8.** Plot of  $-\log(1 - (\alpha_M/R_0 \cdot DP_n))$  versus  $-\log(1 - \alpha_M)$ .

the homopolymer obtained by direct polymerization of **GCMA** (**PGCMA**) was compared to a homopolymer obtained by post carbonation of homopolyGMA (**PGMA**). Thus, carbonation of the homopolymer of glycidyl methacrylate (**GMA**) is another way to obtain **GCMA** homopolymer since the carbonation of epoxide groups allows to obtain easily the corresponding cyclic carbonates with good yield.

In order to synthesize **GCMA** polymers by this way we have first homopolymerized **GMA** in the exactly same conditions than **GCMA** in the previous part: in DMSO 1 M, at 60 °C initiated by AIBN 3 mol%. After precipitation of the polymer and drying under vacuum, the polymer was analyzed by <sup>1</sup>H NMR (see Fig. S6 in Supporting information).

The signals b and b' corresponding to the double bonds of the methacrylate have disappeared after 16 h of polymerization proving that the conversion is complete. The polymer obtained was then carbonated in order to yield **GCMA** homopolymer. The reaction was performed under CO<sub>2</sub> pressure (10 bars) in DMF at 80 °C with LiBr as catalyst. These are the best conditions to obtain cyclic carbonate with very high yield [34]. After 48 h of reaction, the epoxide signals at 3.7 ppm and 4.2 ppm have totally disappeared and the polymer was precipitated in methanol and analyzed by <sup>1</sup>H NMR after drying. NMR analyses (Fig. 9) were identical for both homopolymers of **GCMA** synthesized by carbonation (Route 2) and by direct homopolymerization (Route 1).

Concerning the polymer characteristics (Table 5) a higher molar mass was measured by SEC when **GCMA** was directly homopolymerized. This result is probably a consequence of the chain transfer reaction and the combination reactions on the cyclic carbonate moiety resulting in a branching. Glass transition temperatures of 114 and 134 °C were respectively obtained for the homopolymers of **GCMA** obtained by carbonation and homopolymerization. These values are interesting since it is the first time to the best of our knowledge that a T<sub>g</sub> was measured for such polymers. The difference in the T<sub>g</sub> values can be explained by the difference in the molar masses; the higher are the molar masses, the higher is the T<sub>g</sub>. Moreover, this difference could also be due to crosslinking reactions which can occur during the direct homopolymerization of **GCMA**. All these analyses allow us to conclude that the homopolymerization reaction of **GCMA** monomer was possible in DMSO provided that the monomer concentration was lower than 1 mol L<sup>-1</sup>. Thus we can study more precisely the kinetics of polymerization of this monomer by the determination of the  $k_p^2/k_t$  ratio.

#### 3.4. Determination of the $k_p^2/k_t$ ratio

The determination of the  $k_p^2/k_t$  involves the use of the Tobolsky [56] equation, as used in our laboratory [57], to the homopolymerization of **GCMA** at 60 °C. At this temperature  $kd$ , the initiator rate constant is  $1.13 \times 10^{-5} \text{ s}^{-1}$  [55]. <sup>1</sup>H NMR was used to monitor the **GCMA** conversion (Fig. 10). Two signals at 5.7 ppm and 6.0 ppm were observed for the methylene protons (d and d') of the monomer and a signal at 5.05 ppm corresponding to a mixture of CH (b and g) of the cyclic carbonate moiety both for the



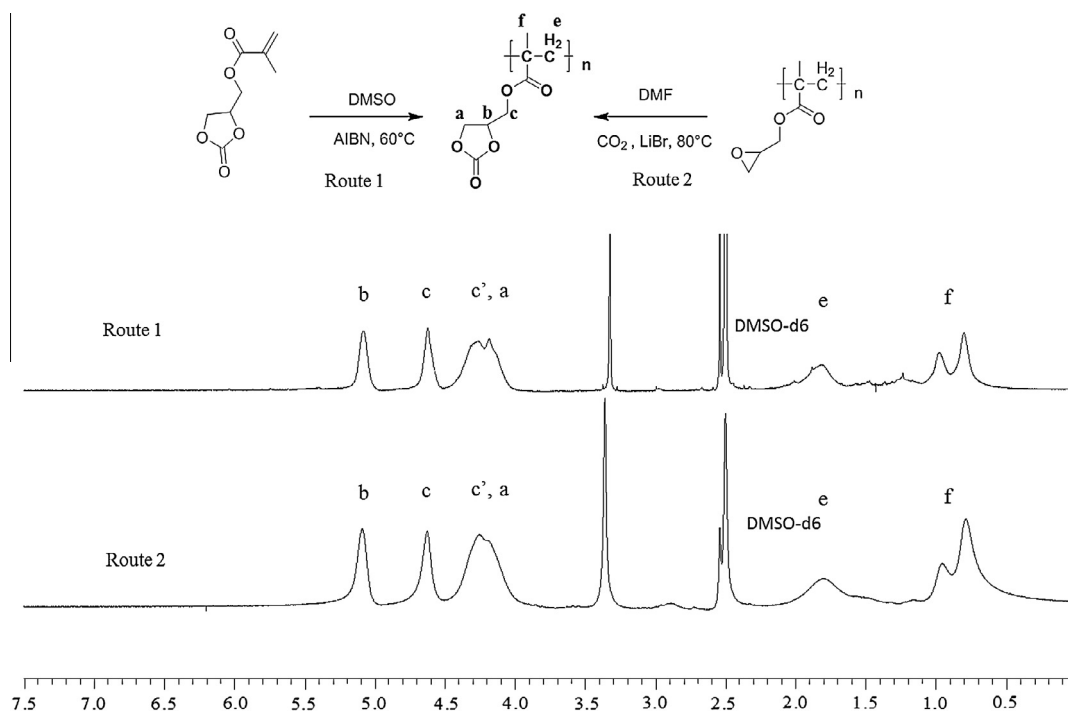


Fig. 9.  $^1\text{H}$  NMR analysis of the homopolymer of GCMA obtained (1) by direct homopolymerization and (2) by carbonation.

Table 5

Characteristics of homopolymers PGMA and PGCMA obtained by carbonation of PGMA (Route 2) and by direct homopolymerization (Route 1).

Run <sup>a</sup>	Mn <sup>a</sup>	Mw/Mn	Tg <sup>b</sup> (°C)
PGMA	33,000	2.1	72
PGCMA (Route 2)	43,000	2.2	114
PGCMA (Route 1)	86,000	2.4	134

<sup>a</sup> Estimated from size exclusion chromatography (SEC).

<sup>b</sup> Estimated from differential scanning calorimetry (DSC).

monomer and the polymer is also observed. I1 is the integration height of d proton of the GCMA double bond and I2 is the integration height of the mixture of CH protons (b and g) of the cyclic carbonate from the monomer and from the homopolymer. I1 is proportional to [GCMA] (monomer concentration in the feed at time  $t$ ) and I2 should be proportional to [GCMA]<sub>0</sub> (initial monomer concentration), thus the ratio I1/I2 is equal to [GCMA]/[GCMA]<sub>0</sub>.

The values are given in Table S1 in Supporting information. A graphical representation of  $\ln([GCMA]/[GCMA]_0)$  versus  $1 - \exp[-(k_d t)/2]$  gives a straight line, the slope of which (42.72) permits us to obtain  $k_p^2/k_t = 245 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  (with the time  $t$ (s)), an efficiency rate  $f=0.7$ ). We also obtained a line slope for the graphical representation of  $\ln([GCMA]/[GCMA]_0) = f(t)$  (See Fig. S7 in Supporting information) which indicated that the polymerization was very fast.

To compare this result in the same conditions with those obtained for methyl methacrylate and other monomers used for coatings synthesis, we calculated in the same way  $k_p^2/k_t$  of three other monomers: MMA, HEA and GMA although  $k_p^2/k_t$  were already [55] calculated for

these monomers in other solvents. These monomers were thus homopolymerized in DMSO ( $1.2 \text{ mol L}^{-1}$ ) at  $60^\circ\text{C}$  during 16 h. For all the polymerizations  $\ln([M]/[M]_0)$  versus  $1 - \exp[-(k_d t)/2]$  has given a line that allowed us to calculate the polymerizability ratio of each monomer, the results are summarized in Table 6.

The reactivity of HEA is higher than that of all methacrylates, since according to Guyot et al. [58], the reactivity difference between acrylates and methacrylates can be explained with two factors. The first one is linked to the steric hindrance of the group in the  $\alpha$  position to the double bond. Actually, the steric hindrance of the methyl group is higher than that of the proton and consequently, the attack of the ethylene bond is more difficult. The second factor is related to the action of the oxygen atom from the carbonyl group of the ester function which can create a charge on the carbon in  $\alpha$  position to the double bond. This charge can be compensated by the donating, inductive effect of the methyl group in the case of the MMA. Furthermore, we have also observed that GCMA reactivity value was 1.7 times higher than that of MMA value and 7 times higher than that of GMA in the same conditions. The high reactivity of acrylate and methacrylate bearing cyclic carbonate moieties was already been demonstrated by Bowman et al. [59–62] and by Decker et al. [63–65] in photopolymerization. They found that monomers such as GCMA polymerize more rapidly than classical methacrylate monomers and according to them the cyclic moiety was responsible of this increase in reactivity. Herein we demonstrated for the first time a similar behavior of GCMA in conventional radical polymerization than in photopolymerization.

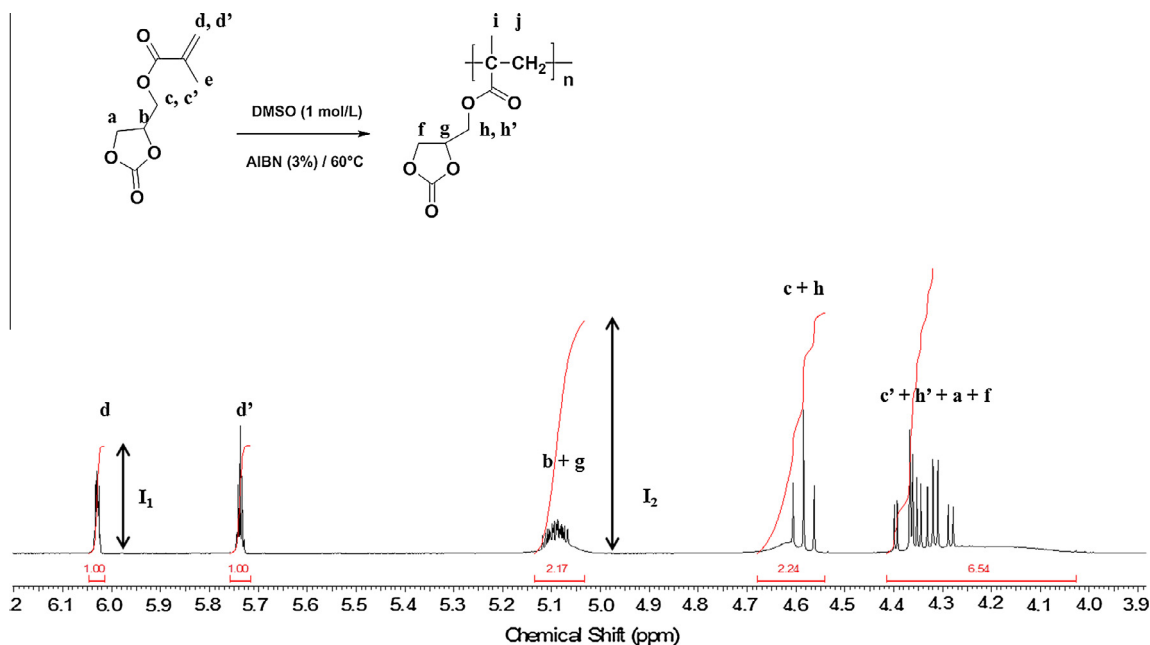


Fig. 10.  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) evolution of GCMA homopolymerization at 60 min.

Table 6

$k_p^2/k_t$  values in DMSO at 60 °C for GCMA, HEA, MMA, and GMA calculated in this study.

Monomer	$k_p^2/k_t$ ( $10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ )
HEA	731
GCMA	245
MMA	149
GMA	37

### 3.5. GCMA and MMA reactivity ratio

The high reactivity of GCMA in DMSO was clearly demonstrated thanks to the  $k_p^2/k_t$  determination. Herein we determined the reactivity of GCMA in copolymerization in respect with a common methacrylic monomer used in coating formulation such as MMA. The calculation of the reactivity ratios  $r_{\text{GCMA}}$  and  $r_{\text{MMA}}$  of each monomer is a choice way to evaluate the capacity of monomers to copolymerize. Among several procedures available to determine monomer reactivity ratio, we chose Macret's method [66]. Indeed this method allows the determination of  $r_1$  and  $r_2$  from a single experiment whereas some other methods require more experiments and the use of each monomer in excess in regard with the other. In this article we have already showed that transfer reactions to cyclic carbonate can occur at high concentration, therefore for this study only MMA was put in excess. Macret's method is a graphical method which was described by Ezrielev et al. [67] and is represented by the following equation (Eq. (5))

$$\frac{X}{Y}(Y-1) = -r_2 + r_1 \frac{X^2}{Y} \quad (5)$$

where  $X = [\text{M1}]/[\text{M2}]$ , which is the monomer concentration ratio in the reaction medium, and  $Y = d[\text{M1}]/d[\text{M2}]$ , which

is the comonomer concentration incorporated in the copolymer as a function of time. The  $X$  value can be easily calculated whereas the  $Y$  value is more difficult to obtain. Considering that the consumption of monomer is a first-order reaction, one can write Eqs. (6)–(8):

$$[\text{M}_i]_t = [\text{M}_i]_0 \exp(-\alpha_i t) \quad (6)$$

and consequently

$$d[\text{M}_i] = -\alpha_i [\text{M}_i] dt \quad (7)$$

so

$$Y = \frac{d[\text{M1}]}{d[\text{M2}]} = \frac{\alpha_1 [\text{M}_1]}{\alpha_2 [\text{M}_2]} \quad (8)$$

Thus,  $\alpha_i$  can be determined by plotting  $\ln([\text{M}_i]_0/[\text{M}_i])$  versus time (Fig. 11), with  $\alpha_i$  representing the conversion rate of  $\text{M}_i$ . For this determination, two copolymerizations with an excess of MMA were performed: The first one with 10% of GCMA and 90% of MMA ( $f_{\text{GCMA}} = 0.1$  and  $f_{\text{MMA}} = 0.9$ ) and the second one with 20% of GCMA and 80% MMA ( $f_{\text{GCMA}} = 0.2$  and  $f_{\text{MMA}} = 0.8$ ). The copolymerizations of GCMA with MMA were carried out in DMSO (1 M) at 60 °C with 1% (molar ratio) of AIBN. The values of  $\alpha_{\text{GCMA}}$  and  $\alpha_{\text{MMA}}$  were determined to be  $5.2 \times 10^{-3}$  and  $2.4 \times 10^{-3}$  for  $f_{\text{GCMA}} = 0.2$ .

The values of  $r_{\text{MACG}}$  and  $r_{\text{MMA}}$  were calculated by plotting  $X(Y-1)/Y$  versus  $Y^2/Y$  and were found to be 0.5 and 2.01 respectively (Fig. 12).

The same calculations were performed for the experiment with  $f_{\text{GCMA}} = 0.1$ , all the results were summarized in Table 7.

We can conclude from these results that the GCMA and MMA reactivity coefficients are different in DMSO so the copolymerization of these two monomers does not occur as in the ideal case.  $r_{\text{GCMA}}$  is four times higher than

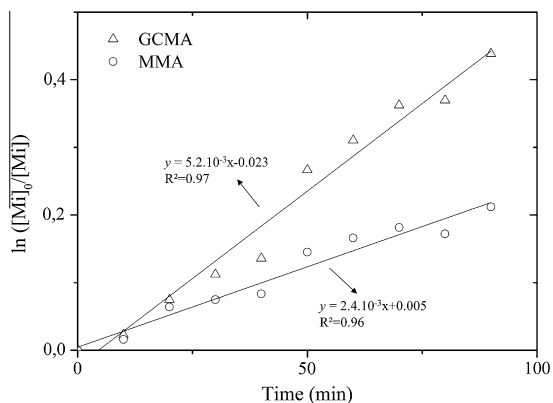


Fig. 11. Macret plot for determining  $\alpha$  values with  $f_{GCMA} = 0.2$ .

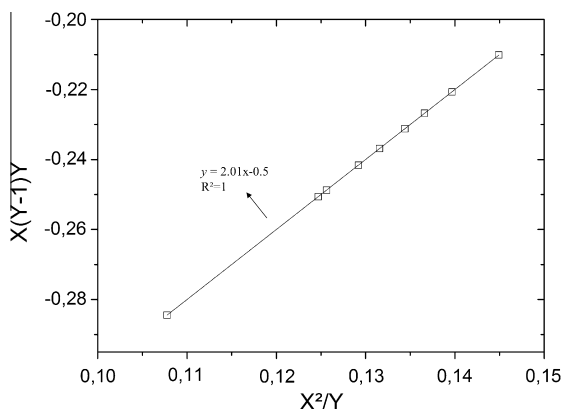


Fig. 12. Macret plot for determining reactivity ratios with  $f_{GCMA} = 0.2$ .

Table 7

$\alpha_{GCMA}$ ,  $\alpha_{MMA}$ ,  $r_{GCMA}$  and  $r_{MMA}$  values for the various  $f_{GCMA}$  values.

$f_{GCMA}$	$\alpha_{GCMA}$	$\alpha_{MMA}$	$r_{GCMA}$	$r_{MMA}$
0.1	$3.6 \times 10^{-3}$	$1.8 \times 10^{-3}$	2.0	0.5
0.2	$5.2 \times 10^{-3}$	$2.4 \times 10^{-3}$	2.1	0.5

$r_{MMA}$ , this means that **GCMA** growing radicals have higher tendency to react with other **GCMA** radicals rather than **MMA** radicals and **MMA** radicals preferably react with **GCMA** radicals rather than other **MMA** radicals.

#### 4. Conclusion

This work reports the synthesis of polymers starting from glycerin carbonate methacrylate. The better way to synthesize this monomer is the carbonation way which can provide a better purity than the transesterification way that gives by-products. Homopolymerization of **GCMA** was succeeded in DMSO but a maximum concentration of 2 M is required in order to obtain polymers with correct PDI. Indeed, transfer reactions to cyclic carbonate were highlighted, leading to cross-linked polymers with high concentration of **GCMA**. Taking into account these results, kinetic studies of this monomer were performed: reactivity ratios with **MMA** and the  $k_p^2/k_t$  constant proved a high

reactivity of this monomer which is 1.7 times higher than that of **MMA**. Therefore conditions of homopolymerization and copolymerization must be monitored in order to obtain desired polymers with reactive cyclic carbonate moieties.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2014.10.001>.

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