

## Synthesis and applications of unsaturated cyclocarbonates

Cite this: *Polym. Chem.*, 2013, **4**, 4545

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Great attention has always been paid to monomers bearing at least two reactive groups, one for copolymerization and one for further reaction, in particular, for cross-linking. Such reactive groups should be reactive enough for crosslinking but should not prevent any copolymerization of monomers. Cyclic carbonate groups are currently gaining increasing attention both from academic and industrial communities. Indeed, these functions allow better control in terms of spontaneous crosslinking reactions than other reactive groups and could also come from renewable resources such as glycerine or CO<sub>2</sub>. Although many papers report the use of cyclic carbonates for synthesis of linear polyurethanes, this present review is the first one that focuses on the synthesis and use of functional cyclocarbonate molecules. In the first part, the present review goes into details of the synthesis of carbonate groups. In the second part, this review is dedicated to the synthesis and the application of various monomers bearing cyclic carbonate groups to polymers.

Received 13th March 2013

Accepted 17th April 2013

DOI: 10.1039/c3py00343d

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### 1 Introduction

The synthesis of materials with interesting mechanical properties requires the use of polymers of high molecular masses or the direct or post-polymerization crosslinking of oligomers after the material formation. This review concerns this second

class of materials. Therefore monomers with two different reactive groups are needed: the first one corresponding to the unsaturated double bond of the monomer is intended to copolymerize with other comonomers, while the second one, the carbonyl of the cyclic carbonate, induces the crosslinking reaction. For example, we could mention the vinylic monomer, copolymerizable by radical polymerization, with a reactive epoxide (or isocyanate) function. This field of research is of great importance and our group has already published a general review article on this subject.<sup>1</sup> The number of reactive groups is not relevant since the reaction needs to be easy to

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working as a post-doc and member of the team "Ingénierie et Architectures Macromoléculaires" (IAM). His current research focuses on the design and synthesis of functional monomers, the synthesis of biobased polymers and their characterization.

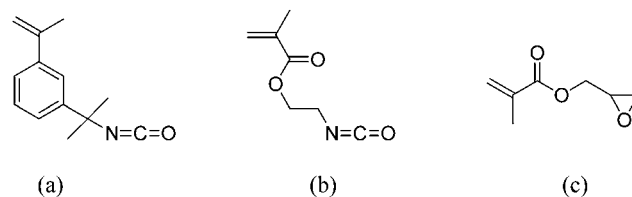


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tional polymers by radical polymerization; the characterization of the polymers and the evaluation of their properties are also considered. She is also looking for new solutions in the synthesis of green functional polymers.

process and non-balanced (acid and alcohol groups are excluded). Moreover, these reactive groups should not inhibit any oligomer synthesis. Several reactive groups were extensively reported such as amines, epoxides and isocyanates. However, concerning amines, few works are reported, mainly on account of the Michael addition side-reaction on electron-poor monomers [particularly (meth)acrylic].<sup>2</sup> Concerning isocyanates, Dimethyl Meta Isopropenylbenzyl Isocyanate (TMI, Fig. 1a) is commercially available but exhibits a low reactivity. Methacryloyloxyethyl isocyanate (EMI, Fig. 1b) is widely used in academic research but is not produced on an industrial scale. Finally, concerning epoxide monomers, glycidyl methacrylate (GMA, Fig. 1c) is largely used in industry but exhibits high toxicity and is very expensive, which reduces its development.

Another reactive group is currently gaining a great deal of attention. This method allows the use of cyclic carbonate groups which leads to less harmful monomers but with a lower reactivity, which allows better control of crosslinking than with



**Fig. 1** Chemical structures of (a) Dimethyl Meta Isopropenylbenzyl Isocyanate (TMI), (b) Methacryloyloxyethyl isocyanate (EMI) and (c) Glycidyl MethAcrylate (GMA).

isocyanate or epoxide functions (spontaneous crosslinking reactions). This review article displays all the monomers bearing both double bonds polymerizable by radical polymerization and cyclic carbonate groups, reports the synthetic method of these monomers and studies the influence of the cyclic carbonate group on the polymerization of the double bonds.



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*monomers and polymers. Recently, he is interested in the synthesis of new biobased building blocks and polymers. Now Professor Emeritus, he has been co-director of more than 200 PhD theses, co-author of more than 250 patents and 1000 articles.*

## 2 Carbonate functions synthesis

In this part, carbonation methods will be briefly reported. The first part is dedicated to the synthesis of aliphatic cyclic carbonates whereas the second part deals with the synthesis of cyclic carbonates bearing reactive groups.

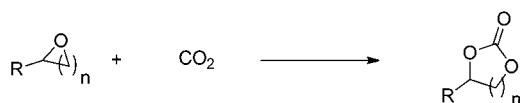
### 2.1 Aliphatic cyclic carbonates synthesis

The first synthesis of cyclic carbonates was reported by Carothers *et al.*<sup>3–5</sup> in the early 1930s. This work was focused on the synthesis of cyclic carbonates by high temperature depolymerization of linear polycarbonates with various catalysts. Nowadays, six (and more)-membered cyclic carbonates are still synthesized either by depolymerization of aliphatic oligocarbonates or from linear carbonates.<sup>6,7</sup> The best yields and selectivities are obtained with the reaction of carbon dioxide on cyclic ethers with catalysts such as Lewis acid–bases and ammonium or phosphonium salts. Other efficient catalysts are reported in several articles (Scheme 1).<sup>8–67</sup>

The research of synthetic routes with less and less environmental impact led to the synthesis of cyclic carbonates in ionic liquids activated by microwaves.<sup>68–71</sup> Silica-supported ionic-liquids exhibited various advantages,<sup>72–84</sup> such as high efficiency,<sup>85–100</sup> high reactivity, an easy purification<sup>101</sup> and the possibility of reusing the catalyst three times without activity loss or by-product formation.<sup>102</sup>

### 2.2 Synthesis of cyclic carbonates bearing reactive groups

Carbon dioxide could be used under supercritical conditions,<sup>103</sup> with<sup>54,55,104–111</sup> or without any catalyst.<sup>112</sup> Supported catalysts could have been reused.<sup>113–124</sup> Silica-supported onium salts have a catalytic activity 100 times higher than non-supported salts. The synthesis of cyclic carbonate groups by co-cyclization between alkenes or alkynes and carbon dioxide exists, but this reaction was little studied.<sup>125–128</sup> Cyclic carbonate groups could be obtained by electrochemical reactions<sup>129–131</sup> with high yields,<sup>29,132</sup> and even with quantitative yield.<sup>133</sup> Following these routes, cyclic carbonates with epoxide function<sup>134–137</sup> or *syn*-diol<sup>138</sup> could be synthesized. Purification is performed by filtration on silica or alumina to absorb nitrogen and halogen impurities.<sup>139</sup> Moreover, cyclic carbonates could be easily synthesized by transesterification of a hydroxyl reactant (or polyhydroxyl) with dialkyl carbonates (diethyl or dimethyl carbonates)<sup>140–144</sup> with basic catalysts.<sup>145</sup> Phosgene and derivatives could also be used.<sup>146</sup> Depending on the targeted cyclic carbonate, various hydroxyl reactants were used, such as mannitol,<sup>147</sup> catechol,<sup>148–150</sup> 1,3-propanediol,<sup>151–157</sup> trimethylolpropane,<sup>158,159</sup> 2,2'-biphenol or 1,1'-bis(2-naphthol).<sup>160</sup> The synthesis of seven (or more)-membered cyclic carbonates is



**Scheme 1** Carbonatation reaction of oxirane ( $n = 1$ ) and oxetane ( $n = 2$ ).

generally carried out by transesterification.<sup>161–164</sup> An eighteen-membered cyclic carbonate was even reported by Weilandt *et al.*<sup>162</sup> In addition, cyclic carbonates were synthesized by carbon dioxide carbonation of allylic alcohol derivatives.<sup>165–176</sup> Even though the synthesis of cyclic carbonates was first reported in the 1930s, the synthesis of five-membered (or more) cyclic carbonates is gaining increased attention, with several studies of various substrates.

## 3 Synthesis and applications of monomers

Some articles report the synthesis of polymerizable monomers bearing cyclic carbonate groups. Thus this review is not dedicated to the synthesis method but is focused on structures of monomers (with various natures of double bonds) and their use in polymerization, from the most unusual monomers to the most usual ones (acrylics and derivatives).

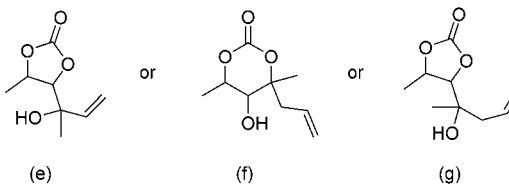
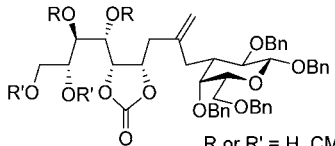
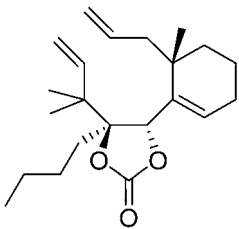
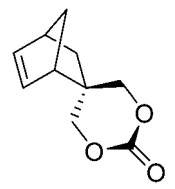
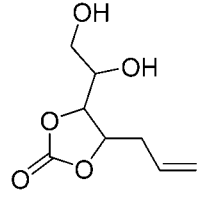
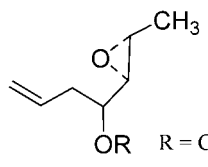
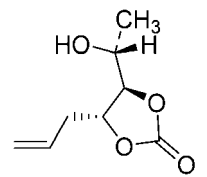
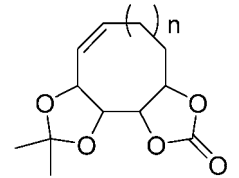
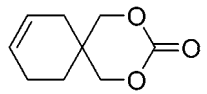
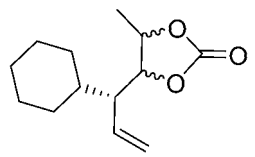
### 3.1 Unusual monomers

Special molecules bearing cyclic carbonate groups are used in various applications, not only in polymers. Thus, for health applications, monomers with saccharide groups are carbonated from diphosgene (Table 1g).<sup>176</sup> A carbonated molecule was also reported as an intermediate in the synthesis of taxol (Table 1h).<sup>178,179</sup> Hanna and Ricard<sup>180</sup> synthesized new 7- and 8-membered carbo-cyclic carbonates and the corresponding dienes from galactose by ring-closing metathesis (RCM), with Grubbs catalyst (5 mol%, 0.06 M) in dichloromethane (Table 1i). Chen *et al.*<sup>181</sup> studied the synthesis of 2,2-(2-pentene-1,5-diyl)-trimethylene carbonate (HTC) and its behavior in polymerization by the condensation of ethyl chloroformate and the corresponding 1,3-diol (Table 1m). Kühling *et al.*<sup>182</sup> reported the polymerization of 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (BCH-cyclocarbonate) (Table 1i) by anionic ring opening polymerization, by a thorough study on the structure of intermediate anions (*endo* or *exo*) in the cycle. The anion is randomly in the *endo* or *exo* position, which leads to an atactic polymer. Lombardo *et al.*<sup>183</sup> synthesized an allylic cyclic carbonate (Table 1n) from bis-trichloromethyl carbonate with an interesting yield of 94%. Roush *et al.*<sup>184</sup> studied various saccharides, with the synthesis of peculiar cyclic carbonates. Thus, during the synthesis of 2-deoxyhexose, the authors obtained a cyclic carbonate diol with high yield from epoxide containing *tert*-butyldiphenylsilyl (TBDPS) ethers (Table 1j). For the synthesis of mycarose,<sup>185</sup> epoxide reactant leads to three different cyclic carbonates [(d), (e), (f), Table 1]. Finally, during the synthesis of a special saccharide, Roush and Brown<sup>186</sup> synthesized following allylic cyclic carbonate (Table 1k).

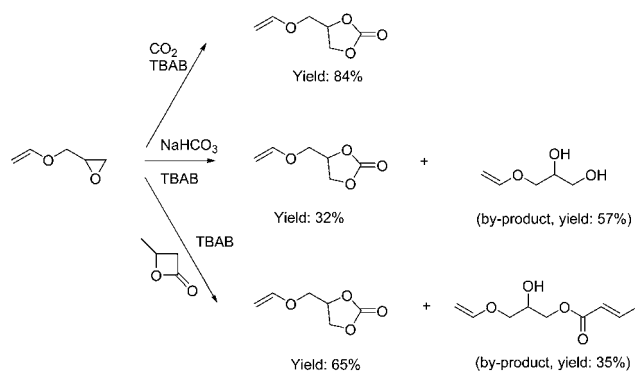
### 3.2 Vinyl ether monomers

To the best of our knowledge, the first synthesis of vinyl ethers bearing cyclic carbonate groups was reported in 1994 by Nishikubo *et al.*<sup>187</sup> by three different routes (Scheme 2). This synthesis was carried out through reaction of glycidyl vinyl ether (GVE) with three different reactants ( $\text{CO}_2$ ,  $\beta$ -butyrolactone or sodium hydrogenocarbonate) in toluene, with

**Table 1** Structures of some unusual cyclocarbonates

Molecule	Authors	Conditions	Carbonates
d, e, f	Roush <sup>185</sup>	(1) Et <sub>2</sub> AlCl, Et <sub>2</sub> O, −20 °C, (2) 1N H <sub>2</sub> SO <sub>4</sub> , yield: 75%	 (e) or (f) or (g)
g	Notz <sup>177</sup>	From the corresponding acetones: (1) THF: H <sub>2</sub> O : TFA = 5.5 : 2 : 2, heat, 50 min, yield: 69%, (2) then Ac <sub>2</sub> O/py for acetylated compounds, quantitative	 R or R' = H, CMe <sub>2</sub> , Ac
h	Ma, <sup>178</sup> Schiltz <sup>179</sup>	Multi-step synthesis, yield: 75%	
i	Kühling <sup>182</sup>	Unknown, produced by Bayer AG	
j	Roush <sup>184</sup>	(1) Et <sub>2</sub> AlCl, Et <sub>2</sub> O, −20 °C, (2) aq. H <sub>2</sub> SO <sub>4</sub> , yield: 69%	
k	Roush <sup>186</sup>	 R = CONHC <sub>6</sub> H <sub>5</sub> (1) BF <sub>3</sub> O(Et) <sub>2</sub> , Et <sub>2</sub> O, 0 °C, 1 h, (2) H <sub>2</sub> SO <sub>4</sub> (1N), 23 °C, 3 h, yield: 80%	
l	Hanna and Ricard <sup>180</sup>	$n = 1$ , RT, yield: ~90%, $n = 2$ , 40 °C; yield: 95%	
m	Chen <sup>181</sup>	Et <sub>3</sub> N, THF, 0 °C, 2 h, yield: 81%	
n	Lombardo <sup>183</sup>	From the corresponding diols: bis(trichloromethyl)carbonate, Et <sub>3</sub> N, CH <sub>2</sub> Cl <sub>2</sub> , RT, <i>cis</i> : yield: 90%; <i>trans</i> : yield: 94%	





**Scheme 2** Different synthetic routes of (2-oxo-1,3-dioxolan-4-yl) methyl vinyl ether (OVE) from vinyl glycidyl ether.

tetrabutylammonium bromide (TBAB) as the catalyst. With  $\text{CO}_2$ , the conversion yield of (2-oxo-1,3-dioxolan-4-yl)methyl vinyl ether (OVE) is between 47 and 84%, and increases with temperature (from 80 to 100 °C), reaction time (from 10 h to 24 h) and catalyst concentration (between 1 and 10 mol%). With sodium hydrogenocarbonate, the reaction is performed at 80 °C during 24 to 48 h and led to a best yield of 32%, with 57% of 1,2-dihydroxy vinyl ether as the by-product. With  $\beta$ -butyrolactone, the reaction was carried out at 100 °C yielding 65% of OVE and 35% of (1-hydroxy-3-vinyloxy) propyl crotonate as by-product.

Among the three reported methods of OVE synthesis, the one involving  $\text{CO}_2$  leads to the highest yield. The authors also reported the polymerization of OVE from various routes. OVE was polymerized by cationic polymerization. Two solvents were tested, dichloromethane and toluene. Dichloromethane is a better solvent, since toluene leads to precipitation of the polymer for temperatures below  $-30$  °C. Several catalysts were tested:  $\text{I}_2$ ,  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{BF}_3\text{O}(\text{Et})_2$ .  $\text{BF}_3\text{O}(\text{Et})_2$ , the more acidic one, leads to the best yields. Eventually, in dichloromethane at  $-50$  °C, with  $\text{BF}_3\text{O}(\text{Et})_2$  as the catalyst, P(OVE) polymer was obtained within one hour in 93% yield. Authors also studied the radical polymerization of OVE with electron-acceptor monomers such as methylacrylate (MA), acrylonitrile (AN),<sup>188</sup> *N*-phenylmaleimide (NPM) and maleic anhydride (MAH). Finally, P(OVE) was reacted with various amines such as benzylamine and butylamine (Scheme 3). Butylamine was the most reactive and led to yields of 96% at 80 °C.

Moon *et al.*<sup>189,190</sup> also investigated the synthesis of OVE by carbonation and proceeded to the study of the catalysis and kinetics of the reaction. They used quaternary ammonium salts as catalysts and showed that tetraoctylammonium led to the

best results. Then they studied the copolymerization of OVE with *N*-phenylmaleimide. They estimated reactivity ratios:  $r_{\text{VE}} = 0.52$  and  $r_{\text{M}} = 2.24$  both by the Finneman–Ross and Kelen–Tudos methods. These ratio values are surprising since these couples are known to lead to alternate copolymers. However, the resulting polymers exhibited interesting molar masses of  $M_n$  (about 53 000 g mol<sup>-1</sup>) and a  $T_g$  value of 32 °C. These polymers were miscible to PVC [poly(vinyl chloride)] and SAN [poly(styrene-acrylonitrile)] whatever their concentrations. As far as our team is concerned, we have synthesized this OVE monomer by transesterification of glycerin carbonate and ethyl vinyl ether, with  $\text{Pd}(\text{OAc})_2$  used as the catalyst.<sup>191,192</sup> 1,10-Phenanthroline was used as the ligand. The monomer was synthesized with a yield of 45% (Scheme 4).

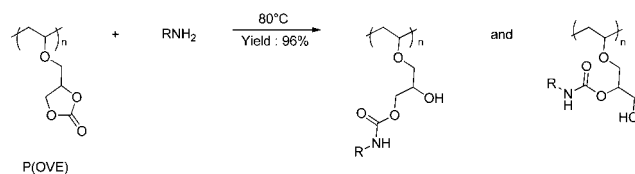
This monomer was then copolymerized with trifluorochloroethylene, hexafluoropropylene and perfluoromethylvinylether and perfectly alternated copolymers were obtained (Scheme 5). We used 5 mol% of *tert*-butylperoxypivalate (TBPI) as the initiator, in order to reach lower molar masses, for lithium ion battery applications.

### 3.3 Vinylic monomers

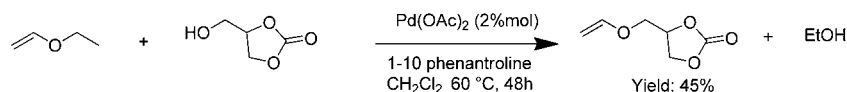
Webster and Crain<sup>193</sup> synthesized a vinyl ethylene carbonate monomer (Fig. 2). They reported the low reactivity of this monomer in radical polymerization, due to its electronic structure. Owing to the vinyl double bond, this monomer is only polymerizable with a vinyl ester and cannot be totally polymerized with acrylic comonomers and hardly copolymerized with styrene. Another similar monomer was synthesized by Bruneau and Dixneuf,<sup>176,194,195</sup> by carbonation of a propargylic alcohol (Scheme 6). This reaction leads to yields ranging between 50 and 100% according to R and R' groups. The best yields were obtained with alkyl groups (98% with R = methyl and R' = ethyl). However, a cyclic carbonate with two double bonds (R' =  $\text{CH}=\text{CH}_2$ ) could be obtained at 130 °C with a yield of 52% if R is a methyl group. Bruneau and Dixneuf<sup>194</sup> reported the synthesis of carbamates, carbonates and oxazolidinones with high yields (not specified) at room temperature from this cyclic carbonate (Scheme 7). The carbamate molecule (o) should be isolated at 0 °C, otherwise it undergoes cyclization at higher temperature to yield the cyclic carbamate molecule (p). If cyclic carbonate reacts with an amino acid in a water/triethylamine mixture, the *N*-blocked derivative (q) is obtained. Molecule (r) can also be obtained by the ring opening reaction of the cyclic carbonate with an amine. Finally, if R' =  $\text{CH}=\text{CH}_2$ , the reaction leads to  $\beta$ -oxopropyl allylic carbonate (s) which is a key-intermediate of Pd-catalyzed allylic alkylation.

### 3.4 Allylic monomers

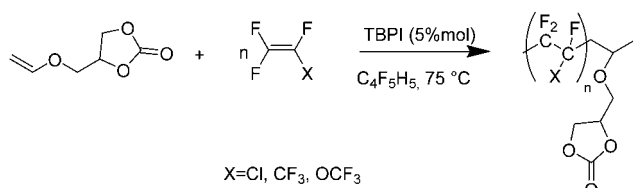
**3.4.1 Allylic cyclocarbonate.** Tomita *et al.*<sup>196–198</sup> compared the reactivity of 5-, 6- and 7-membered allylic cyclic carbonates towards amines. 5-membered allylic cyclic carbonate (5CC) was synthesized by reaction of 1,2-epoxy-5-hexene and  $\text{CO}_2$  with LiBr used as the catalyst. 6-membered cyclic carbonate (6CC) was synthesized from 2-allylpropane-1,3-diol, triphosgene and antipyrine. Concerning the 7-membered cyclic carbonate (7CC),



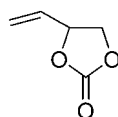
**Scheme 3** Ring opening reaction between cyclic carbonate of P(OVE) and an amine.



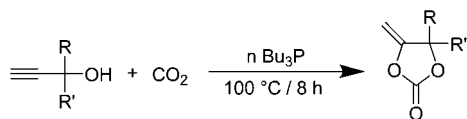
**Scheme 4** Synthesis of 4-(ethenyloxymethyl)-1,3-dioxolan-2-one by transesterification of glycerin carbonate.



**Scheme 5** Radical copolymerization of 4-(ethenyloxymethyl)-1,3-dioxolan-2-one with trifluorochloroethylene (X = Cl), hexafluoropropylene (X = CF<sub>3</sub>) and perfluoromethylvinylether (X = OCF<sub>3</sub>).



**Fig. 2** Chemical structure of 4-vinyl-1,3-dioxolan-2-one (vinyl ethylene carbonate).

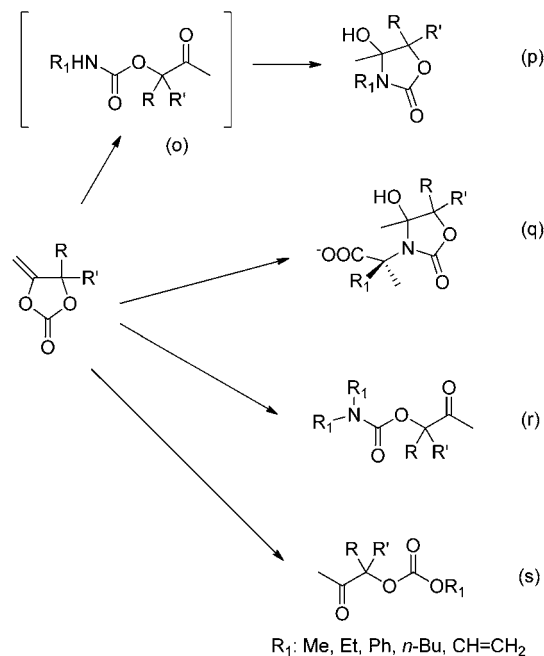


**Scheme 6** Synthesis of 4,4 R,R'-5-methylidene-1,3-dioxolan-2-one from propargylic alcohol derivatives.

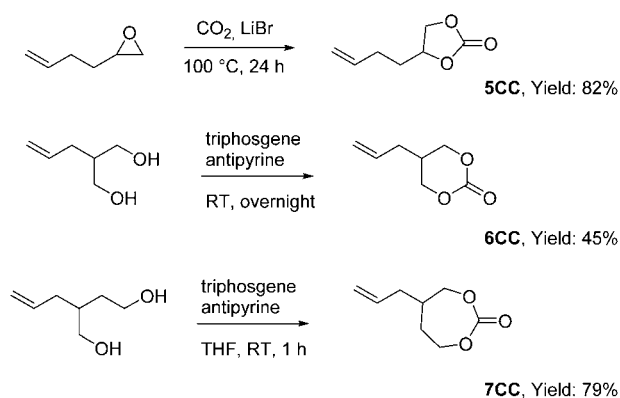
it was synthesized from 2-allylbutane-1,4-diol and triphosgene (Scheme 8).

This same study showed that 6CC is 26 to 60 times more reactive than 5CC with hexylamine. A radical addition of 1,2-ethanedithiol was then performed with AIBN on these allylic cyclic carbonates in order to obtain the corresponding bis cyclic carbonates (B5CC and B6CC) (with respective yields of 53% for B5CC, and 60% for B6CC). Polyhydroxyurethanes [respectively P(B5CC) and P(B6CC)] were then synthesized by step growth polymerization of bis-cyclic carbonates (respectively B5CC and B6CC) with 4,9-dioxadodecane-1,12-diamine (DODDA) at 50 °C in dimethylacetamide (DMAc) (Scheme 9). This study showed that both the conversion yield and molar mass of polyhydroxyurethane (PHU) obtained from B6CC are higher than those from B5CC (Table 2 and Fig. 3). The authors concluded that the higher reactivity of B6CC was due to a higher ring constraint.

After their work on B5CC and B6CC, these authors studied 7-membered cyclic carbonate. 7CC was obtained from the reduction of maleic anhydride in order to get 1,4-diol and ring closing by triphosgene. After 5 h in the same previous conditions, B7CC was obtained in low yield (30% only). Step growth

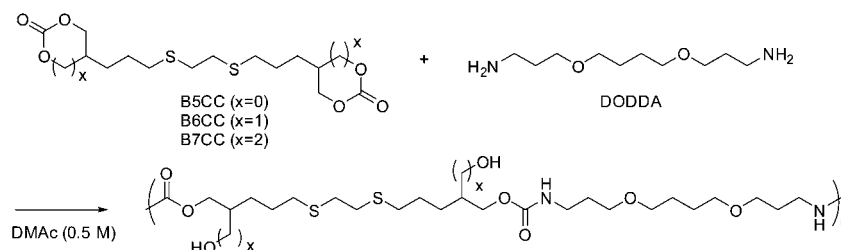


**Scheme 7** Synthetic routes to 4,4 R,R'-5-methylidene-1,3-dioxolan-2-one.



**Scheme 8** Synthesis of 4-(3-butenyl)-1,3-dioxolan-2-one (5CC), 5-(2-propenyl)-1,3-dioxolan-2-one (6CC) and 5-allyl-1,3-dioxepan-2-one (7CC) from allyl epoxide or dihydroxyl precursors.

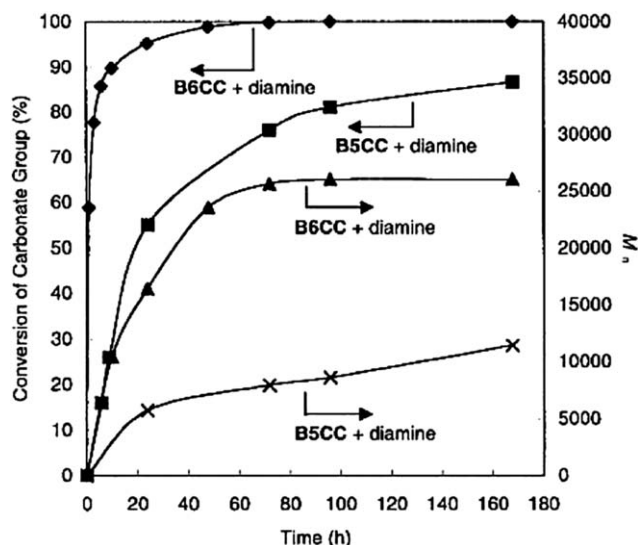
polymerization of B7CC with 4,9-dioxadodecanediamine (DODDA) was carried out in DMSO-d<sub>6</sub> at 50 °C (Scheme 9). Their study highlighted that B7CC was the most reactive cyclic carbonate compared to B5CC and B6CC and led to polymers with highest molar masses ( $M_n = 35\,000\text{ g mol}^{-1}$ ). They estimated the ring constraint energy of three cyclic carbonates and showed that B7CC had the highest energy (5.82 kcal mol<sup>-1</sup> and 2.98 kcal mol<sup>-1</sup> higher than B5CC and B6CC respectively). Thus,



**Scheme 9** Synthesis of a PHU from B5CC (5-membered bis cyclic carbonate), B6CC (6-membered bis cyclic carbonate) or B7CC (7-membered bis cyclic carbonate).

**Table 2** Molar masses and conversion yields of P(B5CC) and P(B6CC)

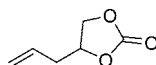
	$M_n$ after 48 h reaction ( $\text{g mol}^{-1}$ )	Yield after 48 h reaction (%)	$M_n$ after 160 h reaction ( $\text{g mol}^{-1}$ )	Yield after 160 h reaction (%)	Activation energy ( $\text{kJ mol}^{-1}$ )
P(B5CC)	8000	70	12 000	85	9.2
P(B6CC)	25 000	95	26 000	100	24.9



**Fig. 3** Conversion yield and molar mass with polymerization time for B5CC and B6CC (reproduced with permission from John Wiley and Sons and Endo *et al.*<sup>198</sup>).

even if the B7CC group is more difficult to synthesize (low yields), it exhibits a high reactivity towards amines and also led to polymers with high molar masses.

Kumar *et al.*<sup>199</sup> studied the optimization of allylic cyclic carbonate synthesis from epoxy reactant and  $\text{CO}_2$  (Fig. 4). They obtained it in 90% yield in 3.5 h at 100 °C with dimethyl carbonate and tetrabutylammonium bromide (TBAB). Moreover, the catalyst and the solvent are reusable and efficient for six successive reactions.



**Fig. 4** Chemical structure of 4-(prop-2-en-1-yl)-1,3-dioxolan-2-one.

**3.4.2 Allyl ether cyclic carbonates.** 4-[(Prop-2-en-1-yloxy)-methyl]-1,3-dioxolan-2-one was synthesized in 1949 by Kropa and Thomas<sup>200</sup> from glycerol- $\alpha$ -allyl ether and either diethyl carbonate<sup>201</sup> or phosgene (Scheme 10). The authors studied its homopolymerization and copolymerization by reacting the allyl double bond, and the materials synthesized therefrom.

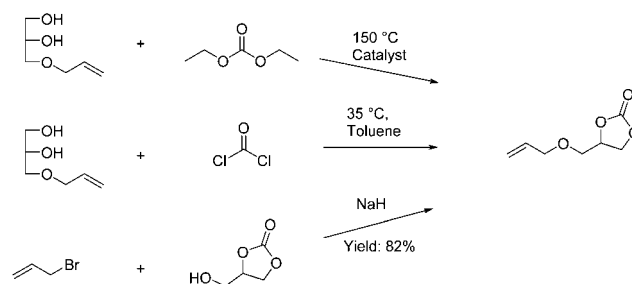
More recently, our team has reported the synthesis of such a monomer<sup>202</sup> by reacting allyl bromide and glycerin carbonate with sodium hydride. Then, we carried out the reaction of this monomer with dithiol (Scheme 11) to lead to bis cyclic carbonate as the precursor of PHU synthesis.

### 3.5 Styrenic monomers

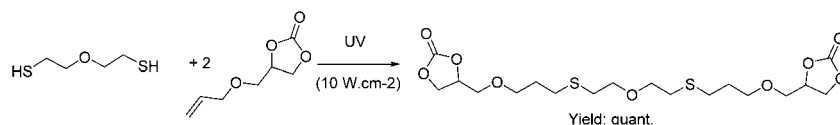
The synthesis of styrenic *para* cyclic carbonate monomers (VBCE) by carbonatation of 4-vinyl-benzyl glycidyl ether (VBGE) with LiBr was studied by Endo *et al.*<sup>203,204</sup> (Scheme 12). Homopolymerization of VBCE leads to a polymer with a molar mass of 26 000  $\text{g mol}^{-1}$  and a  $T_g$  value of 52 °C with a conversion yield of 62%. Copolymerization with styrene yielded statistical copolymers with polymer compositions of monomers similar to that of the starting comonomer compositions. Finally, the authors reported the carbonatation of poly(VBGE) in DMF (Scheme 12). To the best of our knowledge, this is the only example of styrenic monomers and polymers with a cyclic carbonate group.

### 3.6 Vinylene carbonate monomer

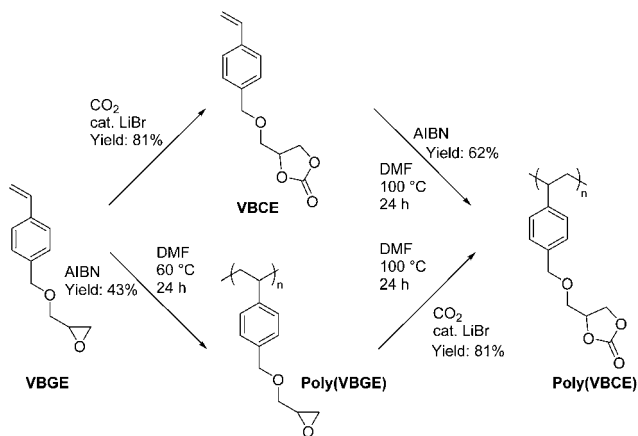
Right from 1955,<sup>205</sup> Newman and Addor synthesized vinylene carbonate (Scheme 13) for further use in the Diels–Alder reaction. The Diels–Alder reaction was successfully performed with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, furane and anthracene. The authors characterized the various structures obtained. Vinylene carbonate (VC) is a commonly



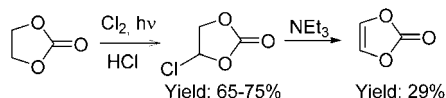
**Scheme 10** Synthesis of allyl ether cyclic carbonate from three different routes.



**Scheme 11** Synthesis of bis cyclic carbonate from the thiol-ene reaction between a telechelic dithiol and allyl cyclic carbonate.



**Scheme 12** Synthesis of poly(VBCE) by polymerization of VBCE or carbonation of poly(VBGE).

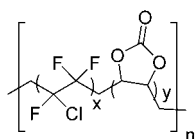


**Scheme 13** Synthesis of vinylene carbonate in a two step reaction from ethylene carbonate.

used electrolyte additive in Li-ion batteries because of its beneficial role in the formation of the solid electrolyte inter-phase. It was shown to contribute to surface film formation on both electrodes of LiCoO<sub>2</sub>/C cells *via* its radical polymerization mechanism.<sup>206</sup>

Vinylene carbonate was used by several authors in direct polymerization.<sup>272-277</sup> Similarly, we have synthesized various polymers from fluorinated monomers and vinylene carbonate.<sup>207,208</sup> Vinylene carbonate and chloro-tri-fluoroethylene (CTFE) (Fig. 5) led to a statistical copolymer with a low molar mass of 2000 g mol<sup>-1</sup>, soluble in polar solvents. Poly(VC-ter-CTFE-ter-hydroxyvinyl ether) copolymer was also synthesized and then acrylated to yield a copolymer soluble in polar and halogenated solvents.

In addition, crosslinked polymers achieved from fluorinated acrylate polymers, reactive diluents and photoinitiators were



**Fig. 5** Poly(VC-co-CTFE) copolymer.

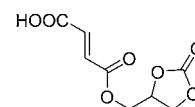
synthesized. After UV-curing, materials were transparent and homogeneous, with interesting thermal and mechanical properties, and a low refractive index required for optic fibers manufacturing.<sup>208</sup>

### 3.7 Maleic carbonate monomer

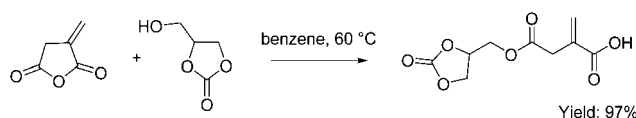
The addition of glycerin carbonate on maleic anhydride led to the monomer sketched in Fig. 6.<sup>209,210</sup> The authors also reported the transesterification of maleate with glycerin carbonate, but high reaction temperature (>100 °C) led to polycondensate by-products.<sup>210</sup> D'Alelio and Huemmer<sup>210</sup> reported that thermal initiators such as benzoyl peroxide could not allow one to reach high conversion polymerization of this monomer. In contrast, copolymers obtained with methyl methacrylate were far richer in methyl methacrylate, and release CO<sub>2</sub> when heated at 155 °C. Hence, after one hour of heating at 155 °C, the polymers were crosslinked. On the other hand, copolymerization with vinyl acetate led to alternating copolymers.

### 3.8 Methyl itaconate carbonate monomer

D'Alelio and Huemmer<sup>210</sup> also studied the methyl itaconate cyclic carbonate monomer (MICC) (Scheme 14). This monomer was synthesized by reaction of glycerin carbonate with itaconic anhydride in benzene with a high yield of 97%. MICC polymerization was easily initiated by a thermal initiator such as benzoyl peroxide. When heated at 135 °C, poly(MICC) releases CO<sub>2</sub> and crosslinks. After one hour of curing, the crosslinked polymer was no longer soluble in toluene or DMF. After curing, infrared spectroscopy revealed a decrease of carboxyl and carbonate absorption bands and the appearance of a hydroxyl absorption band, which tends to explain crosslinking by a transesterification reaction with ring opening of cyclic carbonates, followed by elimination of CO<sub>2</sub> molecules.



**Fig. 6** Chemical structure of (2Z)-4-oxo-4-[(2-oxo-1,3-dioxolan-4-yl)methoxy]-but-2-enoic acid.



**Scheme 14** Synthesis of 4-(2-oxo-1,3-dioxolan-4-yl)methyl itaconate.



### 3.9 Acrylate and methacrylate carbonate monomers

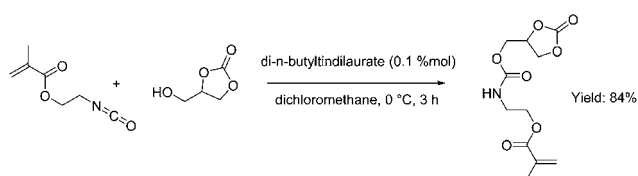
Acrylate and methacrylate carbonate monomers are by far the most studied monomers in the literature. Indeed, they are all highly reactive by radical polymerization to yield functional polymers that are interestingly crosslinkable and suitable for various applications.

**3.9.1 Unusual monomers.** Endo *et al.*<sup>211</sup> synthesized an unusual cyclic carbonate with a carbamate and an acrylate function (Scheme 15). This monomer is synthesized from methacryloyloxyethyl isocyanate which is a very expensive monomer synthesized from a multi-step synthesis. They reported the homopolymerization and copolymerization of this monomer with various acrylates. The most used comonomer, 2-(2-methoxyethoxy)ethyl acrylate, allowed yielding copolymers for applications such as conducting materials in lithium batteries. Properties of synthesized polymers are better than the ones obtained from polymers with glycerin carbonate methacrylate, most probably because of extra carbamate groups.

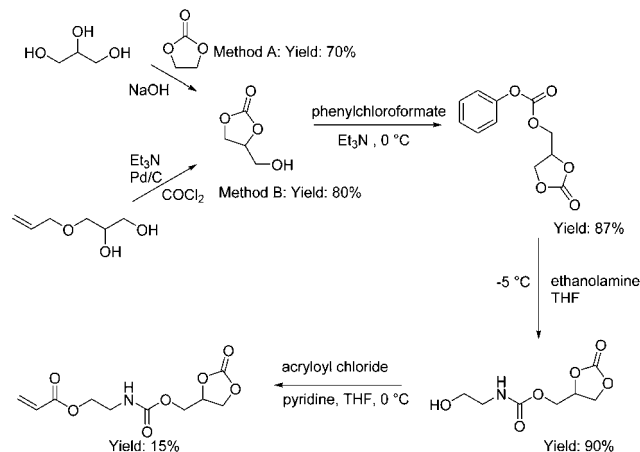
Jansen *et al.*<sup>212</sup> studied the impact of various parameters on the photopolymerization of such acrylate monomers, more particularly the influence of hydrogen bonds. Among the studied monomers, cyclic carbonate carbamate acrylate is particularly interesting since the reactive intermediate for its synthesis could also be a valuable building block. The synthesis of glycerin carbonate from glycerin, in the early steps of cyclic carbonate carbamate acrylate synthesis, is preferentially carried out from allyl glycerin, which allows one to reduce the quantity of residual glycerin and oligomer by-products difficult to remove by distillation (Scheme 16).

Beckel *et al.*<sup>213</sup> studied the influence of a strong acid on the photopolymerization of the double bonds of (meth)acrylate monomers such as cyclocarbonate methacrylate and cyclocarbonate carbamate methacrylate. They showed that the conversion decreased when the acid concentration increased.

**3.9.2 Carbonyl carbonate methacrylate.** In 1990, Brosse *et al.*<sup>214</sup> reported the synthesis of (acryloyloxy)propanediyl-1,2-carbonate and (acryloyloxy-2-ethoxycarbonyloxy)propanediyl-1,2-carbonate in two steps (Scheme 17). The homopolymerization of these two monomers led to insoluble polymers, which precipitated during the reaction. The authors suggest that it arises from a CH transfer on the carbonate group. However, copolymerization with 2-ethylhexyl acrylate is possible for a carbonate monomer concentration lower than 80%. Moreover, the authors estimated reactivity ratios, and the carbonate monomer is much more reactive than the non-carbonate acrylic monomer (respectively  $r_C = 2.65$  and  $r_{acr} = 0.98$  at 0 °C). D'Alelio and Huemmer<sup>210</sup>



**Scheme 15** Synthesis of 2-(((2-oxo-1,3-dioxolan-4-yl)methoxy)carbonyl)amino-ethyl-2-methylprop-2-enoate from glycerin carbonate and methacryloyloxyethyl isocyanate.



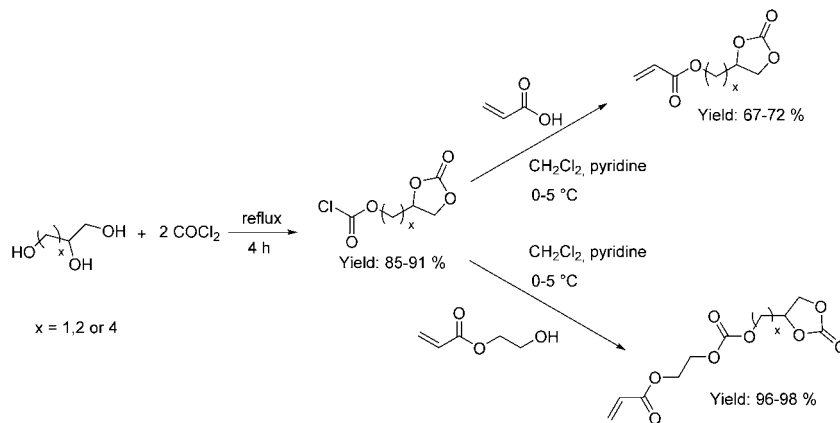
**Scheme 16** Synthesis of 2-(((2-oxo-1,3-dioxolan-4-yl)methoxy)carbonyl)amino-ethyl prop-2-enoate, with reactive intermediates (2-oxo-1,3-dioxolan-4-yl)methyl phenyl carbonate and (2-oxo-1,3-dioxolan-4-yl)methyl (2-hydroxyethyl)-carbamate.

confirmed these results and synthesized copolymers with styrene, vinyl acrylate, methyl methacrylate and other various acrylates. In addition, Wendler *et al.*<sup>215</sup> proposed the use of DMF, instead of toluene, as the polymerization solvent since it is a dipolar aprotic solvent.

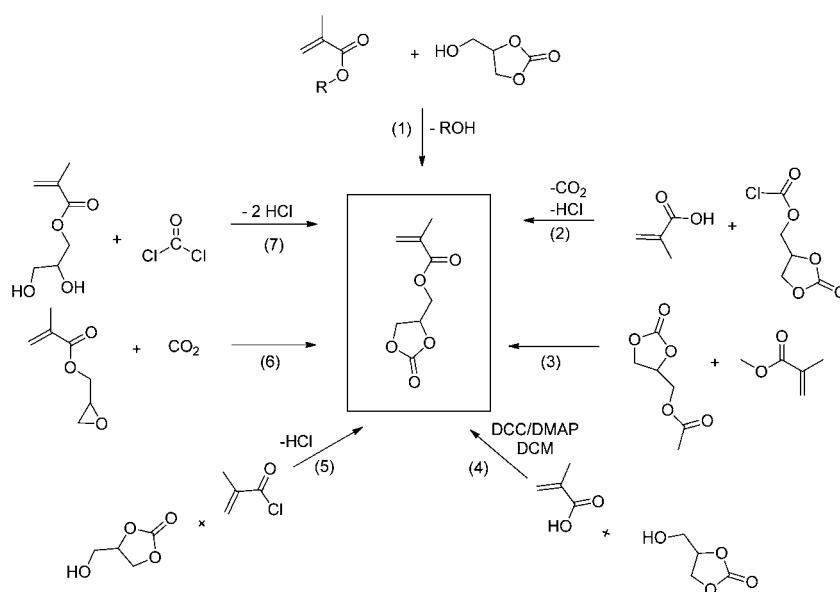
**3.9.3 Glycerin carbonate methacrylate.** This monomer is the most studied monomer, but it is currently commercialized by a few companies like Specific Polymers.<sup>216</sup> In the literature, several synthetic routes have been depicted. In 2003, Webster<sup>217</sup> proposed a summary scheme of the different synthetic routes of this monomer. We completed it with the recent methods reported by Parthiban *et al.*<sup>218,219</sup> and Westfechtel in 2008 (ref. 220) (reactions (3) and (4) in Scheme 18, respectively).

The first synthetic route (1) was reported by Fang in 1961.<sup>221</sup> This route was recently also proposed by Schmitt and Caspari in 2005.<sup>222</sup> Route (2) was first reported by Senet.<sup>223</sup> Carbonation of epoxide route (6) was reported by several teams<sup>225–227</sup> such as Baba *et al.*<sup>228</sup> (in 1987, with  $\text{Bu}_3\text{SnI}-\text{Bu}_4\text{PI}$  as the catalyst), Calo *et al.*<sup>29</sup> (with tetrabutylammonium bromide salts as catalysts) and Wong *et al.*<sup>85</sup> (catalyzed with the tricarbonyl rhenium(i) complex with pyrrolidinium ionic liquid). Synthetic route (7) was first reported by Gallop in 1983,<sup>229</sup> from glycerin methacrylate and phosgene. Yoshikawa *et al.*<sup>230</sup> obtained CCMA according to the synthetic route (5) first depicted by Katz,<sup>231</sup> and then by Beckel *et al.*<sup>52,213</sup> CCMA monomer was then copolymerized with acrylonitrile in toluene in different ratios and initiated by AIBN. Synthesized copolymers were used as chiral recognition materials by adopting Ac-D-Trp or Ac-L-Trp as a print molecule.

Britz, Meyer and Wegner<sup>232</sup> also synthesized CCMA and cyclic carbonate acrylate (CCA) from the synthetic route by Katz.<sup>231</sup> Synthesized monomers were copolymerized by thermal and photoinitiated free radical polymerization with butyl methacrylate (BuMA) and methyl methacrylate (MMA). The authors also tried anionic polymerization in THF initiated with diphenyl lithium but only CCMA could be polymerized.



**Scheme 17** Two step synthesis of (acryloyloxy)propanediyl-1,2-carbonate and (acryloyloxy-2-ethoxycarbonyloxy)propanediyl-1,2-carbonate.



**Scheme 18** Synthetic routes to cyclic carbonate methacrylate (CCMA).

Synthesized copolymers were used as conducting solvents for lithium salts as electrolytes in lithium batteries.

Kihara and Endo<sup>224,233</sup> reported that pure CCMA is unstable but remains stable until 100 °C when non-purified. They showed that chain transfer occurs during CCMA polymerization. They also studied the reaction of poly(CCMA) with an amine and the crosslinking with a diamine. In their review on carbon dioxide and carbon disulfide, Ochiai and Endo<sup>224</sup> depicted two synthetic routes for the synthesis of polyCCMA: the first one corresponds to the polymerization of CCMA, while the second one is based on the polymerization of glycidyl methacrylate followed by the carbonation with CO<sub>2</sub>. Owing to the instability of CCMA, Park *et al.*<sup>234</sup> preferred the homopolymerization of glycidyl methacrylate (GMA) followed by CO<sub>2</sub> carbonation with tetraoctylammonium chloride at 100 °C in DMSO. Endo *et al.*<sup>235,236</sup> favored also the carbonation of poly(GMA) in NMP, with lithium bromide as the catalyst. In both cases, this synthetic route based on carbonation of poly(GMA)

allows the best yields. If thermal free radical polymerization of CCMA raises problems, in particular due to the heat needed to initiate the polymerization, photopolymerization is easier. Therefore, several teams studied this route and, in early 1990, UV (co)polymerization of CCA was reported by Decker and Moussa.<sup>237–240</sup> Their results show that CCA polymerizes more rapidly than classic acrylic monomers. The authors explain this result with the cyclic structure of carbonate, which allows this ultrafast kinetics and enhances the reactivity. They studied the rate of polymerization by infrared spectroscopy and observed that monomers containing cyclic carbonate functions polymerize within milliseconds with high yield. They found that acrylate monomers bearing cyclic carbonate copolymerize with polyurethane-diacrylate more rapidly than conventional mono- and diacrylates and almost as rapidly as triacrylate. Concerning the crosslinked polymers obtained after reaction of the cyclic carbonate function with diamine, they are interesting for protective coating applications. Bowman carried on this

work,<sup>213,241–249</sup> and particularly studied the reactivity and the polymerization kinetics of CCMA and a high number of similar cyclic or urethane bearing monomers in order to prove that the cyclic carbonate moiety is responsible for this high reactivity and not the presence of an arbitrary cyclic structure. The authors explained the high reactivity of these monomers by intramolecular interactions, such as hydrogen bonding, aromatic and heterocyclic ring stacking effects, and intramolecular effects. These studies were also explored by Jansen *et al.*<sup>212</sup> who proposed that the increasing polymerization rate resulted from the increasing dipole moment of the monomer.

The controlled radical polymerization was applied to cyclic carbonate (meth)acrylates by Parthiban *et al.*<sup>218,250</sup> The authors synthesized homopolymers, triblock copolymers and terpolymers bearing cyclic carbonate pendant groups from cyclic carbonate methacrylate by ATRP, using polyethylene glycol macroinitiators. The polymer block bearing carbonate groups is either a homopolymer or a copolymer with methyl methacrylate. Moreover, the authors carried out functionalization of copolymers with amines to crosslink polymers and to study properties such as the conductivity for lithium batteries with bis(trifluoromethane)sulfonide (LiTFSi).

Other teams studied CCMA for its interesting double reactivity and obtained materials with various structures and properties. Figovsky *et al.*<sup>251,252</sup> particularly studied the use of CCMA to elaborate curing-on-demand coatings with diamines. They notably pioneered a new concept of mixed materials between epoxy and polyurethane polymers in which the presence of both hydroxyl and carbamate functions exhibits original properties.

Industrially, CCMA was claimed similarly for various applications. Thus, Iwamura *et al.*<sup>253</sup> synthesized copolymers with both pending cyclic carbonate groups from CCMA and carboxylic groups. They showed the potential for using the cyclic carbonate group of CCMA in automotive coating formulations. Indeed, crosslinking could be carried out either by direct ring opening of cyclic carbonates or by decarboxylation of cyclic carbonates with quaternary ammonium salts to yield the corresponding epoxide that could react with carboxylic acid functions of polymers. Figovsky and Shapovalov<sup>254</sup> also reported the crosslinking of polyacrylates that bear cyclic carbonate functions with polyamines. Stanssens *et al.*<sup>255</sup> and Harui *et al.*<sup>256</sup> also depicted the elaboration of coating by the crosslinking of polymers that bear cyclic carbonates with various amine curing agents.

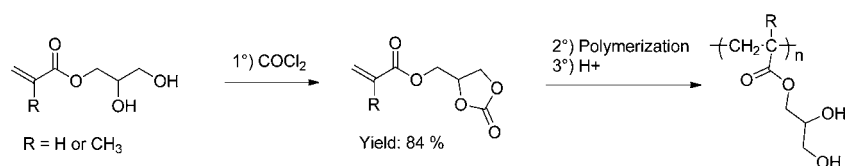
CCMA was also used in emulsion copolymerization. Thus, the synthesis of latex bearing cyclic carbonate functions that could crosslink with primary amines was reported by Yang<sup>257</sup>

from Valspar Company. Other companies such as Rhodia<sup>258</sup> studied cyclocarbonates to propose crosslinking systems without any isocyanates for aqueous coating formulations. BASF Company deeply studied CCMA for paint and coating applications.<sup>259–261</sup> They first reported the synthesis of crosslinkable polymers that bear amine functions with cyclic carbonate curing agents.<sup>262</sup> Then, most of the reported inventions depict crosslinking polymers that bear cyclic carbonates with primary amine curing agents to elaborate paints and coatings with interesting properties without any isocyanates.

These works were completed by those of Anderson<sup>263</sup> who reported the catalysis of cyclic carbonate/amine reactions with strong bases such as potassium *tert*-butoxide to improve the degree of crosslinking of cyclic carbonate acrylic polymers. Besides paints and coatings, other authors reported CCMA in more original applications. Thus, Gallop<sup>229</sup> depicted the use of CCMA in 1983 for hydrogel synthesis. Indeed, after a classic free radical polymerization of CCMA (or CCA) with other acrylics of methacrylic monomers, the copolymer was treated under acidic conditions to decarboxylate cyclic carbonate and yielded a diol function, which was required to synthesize hydrogels (Scheme 19).

Iyer *et al.*<sup>264</sup> reported the radical copolymerization of CCMA with other monomers such as 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MA) or dimethylacrylamide (DMA) to synthesize hydrogels for contact lens applications. These authors used a pioneering synthesis method suggested by Caspari<sup>222</sup> from the transesterification of glycerin carbonate catalyzed by zirconium acetylacetonate. Schiedel *et al.*<sup>265,266</sup> reported the use of CCMA and CCA as surface cleaning agents. Indeed, these monomers have an influence on the wettability of the treated surface, allowing better stain removal, rinsing and drying.

**3.9.4 Glycerin carbonate acrylate.** The synthetic routes to glycerin carbonate acrylate (CCA) (Fig. 7) from acrylates are similar to those described for CCMA from methacrylates. Grahe<sup>267</sup> reported the synthesis of CCA in 1989 from glycerin carbonate acryloyl chloride at a higher temperature than 100 °C. The main drawback consists in the side-reaction of polymerization of reactants and products, despite the presence of inhibitors such as 2,6-di-*tert*-butyl-*p*-cresol. This monomer was also synthesized by Couvret<sup>214</sup> in 1990 by the addition of glycerin carbonate chloroformate and acrylic acid with triethylamine at 0 °C (route (2), Scheme 18). Synthesized carbonic anhydride decomposed in a second step at room temperature, releasing carbon dioxide. After purification, CCA was obtained in 72% yield. D'Alelio and Huemmer<sup>210</sup> studied the synthesis and UV and thermal polymerization of CCA. They synthesized



**Scheme 19** Synthesis of hydrogels from CCMA or CCA precursors.

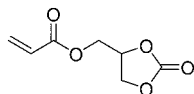


Fig. 7 Chemical structure of (2-oxo-1,3-dioxolan-4-yl)methyl acrylate.

CCA from glycerin carbonate and acryloyl chloride with triethylamine in benzene or dioxane at a temperature between 0 and 5 °C.<sup>210</sup> Purification of CCA is raising problems. In fact, crystallization did not occur and distillation was not possible since CCA polymerizes at 40 °C, even at low pressure close to 10<sup>-4</sup> mm, despite the presence of inhibitors. Their work was completed by Golden *et al.*<sup>268</sup> who synthesized CCA from glycidyl acrylate and CO<sub>2</sub>, at low temperature in the presence of inhibitors with an interesting yield (85%).

As for CCMA, whatever the conditions, all the attempts at solution homopolymerization of CCA led to insoluble polymers that precipitated in the reaction mixture. Couvret *et al.*<sup>269</sup> reported that such insolubility could be explained by the transfer reaction on carbonate rings, with proton removal, followed by a combination of formed radicals (Scheme 20).

The authors showed that insolubility issues could be solved by the copolymerization of CCA with various acrylic comonomers. These copolymers were evaluated as reactive polymers and the use of butylamine allowed functionalization of acrylic copolymers with carbamate pending groups under mild conditions. D'Alelio and Huemmer<sup>210</sup> succeeded in thermal homopolymerization of CCMA with a benzoyl peroxide initiator. However, neither UV photoinitiated polymerization nor crosslinking by post-polymerization succeeded. In contrast, Golden *et al.*<sup>268</sup> showed that CCA could be easily polymerized by UV initiation. After purification by precipitation, poly(CCA) releases CO<sub>2</sub> at 210 °C, whereas, unpurified, it releases CO<sub>2</sub> as soon as 110 °C. Poly(CCA) films were crosslinked at these temperatures, and the crosslinking temperature decreased when acid was added, which suggests that the reaction was catalyzed by acidic conditions. The infrared spectrum of the crosslinked polymer displayed a decrease of carbonate absorption frequency and an increase of epoxide and ether frequencies. These observations may suggest the following mechanism: cyclic carbonate that undergoes a thermal homolytic cleavage which entails CO<sub>2</sub>

elimination, followed either by an epoxide ring formation or a polyether chain addition.

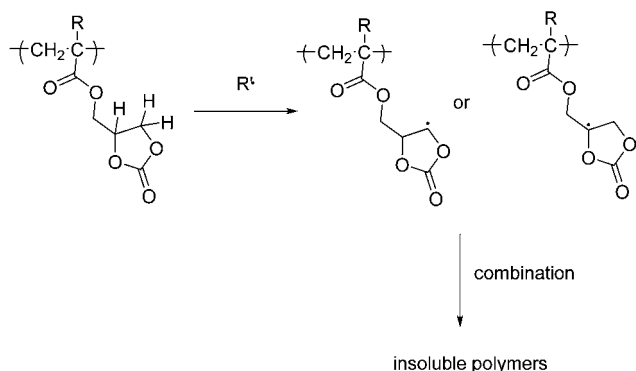
Golden *et al.*<sup>268</sup> studied poly(CCA) with a propylene carbonate plasticizing agent (50% w/w) and obtained a polymer with an interesting low *T<sub>g</sub>* value of -50 °C. After a 12 h wash in water to remove organic solvents, they obtained a gum-like material with good adhesive properties that could absorb again propylene carbonate or DMSO to retrieve elastomeric properties.

## 4 Conclusion

Recent pieces of research from both academic and industrial teams have been reported on the synthesis of unsaturated monomers bearing cyclic carbonate groups. Almost all kinds of double bonds were studied and many polymers were synthesized from these monomers. Various crosslinking reactions, most of them involving amines, were carried out, showing the interest of such a method for post-curing of polymers. The cyclic carbonate group is notably less reactive than the corresponding epoxide group, which allows one to better separate polymerization from crosslinking. However, some side-reactions such as radical transfer to carbonate rings were observed, which usually leads to the synthesis of copolymers with low concentrations of cyclic carbonate monomers. Indeed, cyclic carbonate monomers are really a new and interesting class of reactive monomers that has appeared in recent years, and is increasingly studied for various applications, such as vinyl azlactone<sup>268</sup> or vinyl oxazoline and derivatives.<sup>269-271</sup> However, the reactivity towards various reactants should still be deeply studied to improve the control of crosslinking reactions.

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Scheme 20 Chain transfer reaction during homopolymerization of CCA.



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