

Reactive Applications of Cyclic Alkylene Carbonates

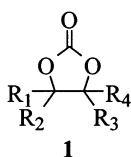
John H. Clements*

Huntsman Petrochemical Corporation, 7114 North Lamar Boulevard, Austin, Texas 78752

The synthesis and use of cyclic alkylene carbonates as reactive intermediates first appeared in the literature more than 50 years ago. However, the range of their usefulness in industrial applications has only been fully realized in the past decade. In this article, numerous reactive applications of the cyclic alkylene carbonates, specifically the five-membered cyclics, are discussed. In addition, utilization of the chemistry presented in this review for the preparation of industrially useful monomers, polymers, surfactants, plasticizers, cross-linking agents, curing agents, and solvents, to name a few, is also discussed.

Introduction

Five-membered alkylene carbonates (1,3-dioxolan-2-ones) of the general structure



have been the subject of considerable research. In particular, ethylene carbonate (EC, $R_{1-4} = H$) and propylene carbonate (PC, $R_{1-3} = H$, $R_4 = CH_3$) have been available commercially for over 40 years.¹ For this reason, much of the following review focuses on research involving these two materials. Since their commercialization in the mid-1950s, EC and PC have found numerous applications as both reactive intermediates and inert solvents. A quick examination of their physical properties (Table 1)² is all that is needed to appreciate why EC and PC are attractive solvent substitutes. In addition to their biodegradability³ and high solvency,⁴ they have high boiling and flash points, low odor levels and evaporation rates,⁵ and low toxicities.⁶ The use of PC as a solvent in degreasing,⁷ paint stripping,⁸ and cleaning⁹ applications has risen dramatically in the past few years. In addition, EC and PC are finding increased utility as diluents for the epoxy¹⁰ and isocyanate¹¹ components of 2K resin systems, and they have become the electrolytes of choice in the production of lithium ion batteries.¹² PC also finds utility as a carrier solvent for topically applied medications and cosmetics.¹³ Although much can be said concerning the use of these alkylene carbonates as inert media, their potential as reactive intermediates is the primary focus of this discussion.

Although a number of methods exist to synthesize five-membered alkylene carbonates of structure 1, carbon dioxide insertion into the appropriate oxirane is the commercial method employed to synthesize the most common of these, EC, PC, and butylene carbonate (BC, $R_{1-3} = H$, $R_4 = C_2H_5$). Typically, an alkylammonium halide catalyst such as tetraethylammonium bromide^{1a,b} is employed (Figure 1). The alkylene carbon-

Table 1. Properties of Ethylene and Propylene Carbonate

property	EC	PC
boiling point (°C)	248	242
freezing/melting point (°C)	36.4	-49
flash point (°C)	160	135
viscosity (cP, 25°C)	2.56 ^a	2.50
% VOC ^b (110 °C)	34	28

^a Supercooled liquid. ^b Volatile organic content.

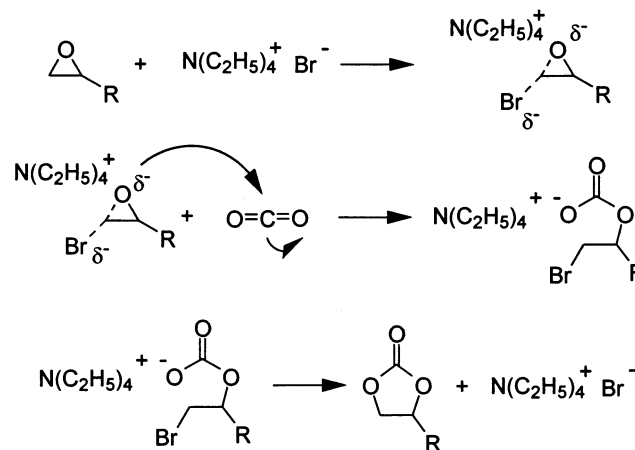


Figure 1. Synthesis of five-membered alkylene carbonates via insertion of CO_2 into oxiranes. $R = H, CH_3, \text{ or } C_2H_5$.

ates produced react with aliphatic and aromatic amines, alcohols, thiols, and carboxylic acids. Under certain conditions, they can also undergo ring-opening polymerization. It is the intent of the author to discuss each type of reaction in detail, from the reaction mechanism and conditions required to a brief description of the applications in which each reaction finds utility. In addition, the synthesis and utility of unique alkylene carbonate derivatives is also discussed. In this way, a general overview of alkylene carbonates as reactive intermediates is intended. Shaikh and co-workers¹⁴ recently published a review of organic carbonates in which several applications of alkylene carbonates are discussed in addition to those of linear carbonates. However, the use of these materials has risen dramatically in the past few years and has grown to encompass several additional areas of active research.

* Tel.: 512-407-0811. Fax: 512-483-0925. E-mail: john_clements@huntsman.com.

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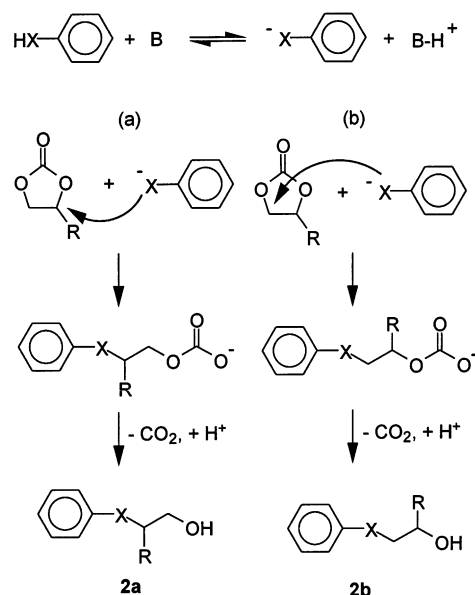


Figure 2. Reactions with aromatic active-hydrogen-containing moieties produces a mixture of isomers **2a** and **2b**. X = O, NH, or S. B indicates to any alkali.

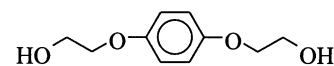
Reactions with Aromatic Amines, Alcohols, and Thiols

Alkylene carbonates, particularly 1,3-dioxolan-2-ones, can be used to alkylate active-hydrogen-containing aromatics such as phenol and phenolic resins,¹⁵ thiophenols,¹⁶ aniline,¹⁷ and the like in the presence of alkali catalysts. The general reaction scheme is illustrated in Figure 2. Note that X can be O, NH, or S. Nucleophilic attack at either alkylene carbon is followed by loss of carbon dioxide to obtain **2a** and **2b** in a 50/50 ± 10 ratio of isomers for R = CH₃. The list of catalysts useful in this reaction is quite long and includes phosphines¹⁶ and phosphonium halides,^{16b} alkali metals,^{15b} tertiary amines,¹⁸ alkali metal halides,^{15a} hydroxides,^{15b} carbonates,^{16a} and alkoxides.^{15b} Typically, temperatures in the range 100–150 °C are required for alkylation of amines and thiols, whereas higher temperatures in the range of 150–200 °C are required for alkylation of alcohols. In such reactions, the alkylene carbonate order of reactivity is R=H > R=CH₃ > R=C₂H₅.

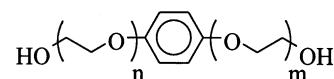
It is well-known that the products shown in Figure 2 can be obtained more directly by reaction with oxiranes such as ethylene oxide (EO) and propylene oxide (PO). The oxiranes are less expensive than their corresponding alkylene carbonates, especially considering that 44 g/mol of carbonate is lost in the form of CO₂ and that alkylation proceeds at lower temperatures. However, alkylene carbonates offer significant advantages over oxiranes in this application. The alkylene carbonates are far less hazardous materials, requiring fewer safety protocols.⁶ In addition, alkylation employing an alkylene carbonate does not require the high-pressure equipment often necessary when working with the highly volatile oxiranes. Most notably, however, is that alkylation employing alkylene carbonates does not require the use of solvent. In most cases, the carbonate acts both as reactant and as solvent. This last advantage is key in the alkylation of aromatic substances that have high melting points or are otherwise difficult to handle.

An illustrative example of alkylation is the reaction of hydroquinone (1 mol) with EC (2 mol) to synthesize

1,4-bis(2-hydroxyethoxy)benzene, commonly known as HQEE¹⁶ 106
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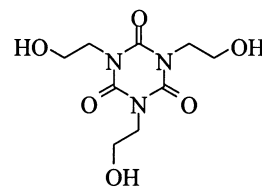


HQEE is a useful spacer in the synthesis of chemically and thermally stable, high-strength polyurethanes that find application in skateboard wheels and tractor tires.¹⁹ Hydroquinone (mp = 172–175 °C) forms a homogeneous liquid with EC when heated to approximately 100 °C. Continued heating to 160 °C gives alkylation and CO₂ evolution, which can be monitored either visually or using a CO₂ analyzer to determine reaction rate and time required. The product, an off-white solid with a melting point of 100–102 °C, can be flaked or handled in the molten state without the added cost of solvent removal. In addition, the alkylene carbonate method is much more selective with respect to the molecular weight distribution of the product obtained. Whereas several moles of EO or PO will react at each site, producing the following material²⁰ 108
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in which $n + m = 0-4$, EC and PC react at each site only once. The result is a product that does not contain ether linkages, a benefit when chemical and thermal stability is desired in the final application. Other examples of alkylation via reaction with alkylene carbonates include the reaction of EC and PC with cardanol (a product derived from cashew nut oil) to produce useful plasticizers²¹ and with resorcinol to produce a lower-melting alternative to the polyurethane spacer HQEE.²² The latter reference features the reaction of resorcinol with EC/PC blends to create a mixture of alkylation products. 124
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An illustrative example of *N*-alkylation is the reaction of cyanuric acid (1 mol) with EC (3 mol) to form 1,3,5-tris(2-hydroxyethyl)isocyanurate (THEIC)¹⁸ 136
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As with hydroquinone, cyanuric acid (mp > 360 °C) forms a homogeneous solution with EC at temperatures well below that required for alkylation to proceed. The product, an off-white solid with a melting point of 136–140 °C, can be prepared without the need for solvent. THEIC is a cross-linking agent employed in the preparation of polyester resins. Resins prepared from this material exhibit the corrosion resistance necessary to coat electrical cables that are laid along the ocean floor. The presence of ether linkages typical of the EO alkylation product would adversely affect the performance of the final product. 139
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Reactions with Carboxylic Acids

Five-membered alkylene carbonates react with carboxylic acids in much the same way as with aromatic active-hydrogen-containing moieties.²³ Similar catalysts 151
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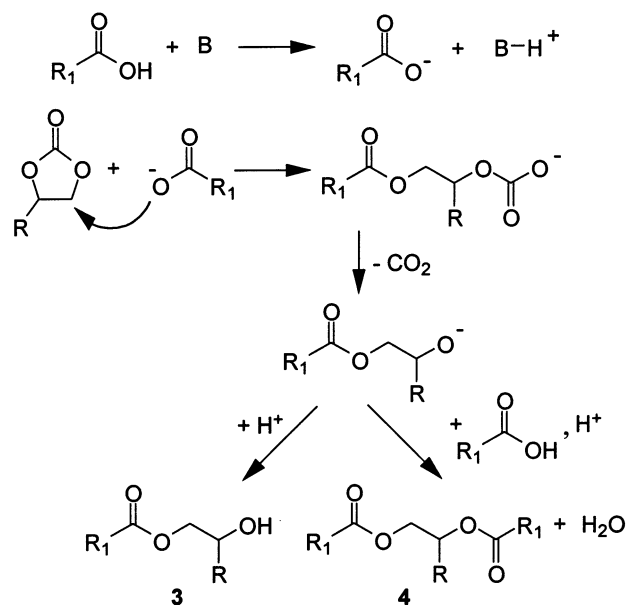


Figure 3. Reactions with carboxylic acids produce a mixture of hydroxyalkyl esters **3** and diesters **4**. Note that only one of two possible isomers of **3** is shown.

and reaction temperatures are required. The reaction is classified as an alkylation/esterification that involves nucleophilic attack at either alkylene carbon (Figure 3). However, a mixture of products **3** and **4** is produced in addition to two isomers of **3** should $R \neq H$. An example is the reaction of benzoic acid with EC. Apicella and co-workers employed a 260% excess of EC to obtain **3** as the predominant product.^{23b} However, Yoshino et al. found that a mere 10% excess could be effective using a triethylammonium iodide catalyst in combination with a shorter reaction time. In this manner, reacting EC with benzoic acid at 140–145 °C for 0.7 h resulted in an 86.5% yield of **3**.^{23a} Although this selectivity represents a drawback to the pure synthetic chemist, it has been exploited to synthesize prepolymers.²⁴ Researchers at Reichhold reacted EC and PC with multifunctional carboxylic acids such as terephthalic acid to synthesize polyester oligomers. These hydroxy-functional oligomers were then reacted with simple diols and unsaturated anhydrides to give unsaturated polyesters useful in composites for the aerospace industry.

In addition to prepolymer synthesis, the above chemistry also finds use in polymer modification. EC has been reacted with poly(ethylene terephthalate) (PET) polyesters in an effort to reduce the acid number of the material. PET polyesters are excellent materials for industrial conveyor belts that operate under heavy loads and at high speeds. However, degradation of the polymer can occur over time, resulting in reduced tensile strength and even visible cracking. Researchers at Allied discovered that a more chemically resistant material could be obtained simply by reacting the polymer with EC, thereby reducing the number of carboxylic acid end groups at which degradation typically occurs.²⁵ The modification procedure follows the polycondensation of dimethyl terephthalate or terephthalic acid with ethylene glycol and involves the addition of an alkali metal salt such as potassium iodide. Typically, 0.5–1.0 wt % EC is added and allowed to react at 280 °C for 5–15 min. The result is a material with an acid number of <3 (mg of KOH/g) as compared to approximately 20 for the untreated polymer. Cape

Table 2. Modification of SAPs with Alkylene Carbonates to Improve AAP Performance

carbonate employed	time at 215 °C	FSC (g/g)	AAP (g/g)
–	–	39	11
EC	15	37	30
PC	20	37	31
PC	30	36	33
BC	20	37	30

Industries has employed PC in a similar application. In this case, the low-acid-number PET material reacts much more quickly with isocyanates to produce polyurethane foams.²⁶ The foams produced exhibit the improved surface adhesion necessary for the production of laminate foam board.

Yet another useful example of polymer modification by reaction with five-membered alkylene carbonates takes advantage of the diester product **4** as a cross-link site. Lightly cross-linked sodium polyacrylate is a hydrophilic material that absorbs many times its weight in water yet does not dissolve. This property makes the material useful as a superabsorbing media for sanitary articles such as diapers and feminine hygiene products.²⁷ However, the liquid-filled material is easily deformed by an external pressure such as the sitting action of a child, resulting in unwanted discharge of the absorbed liquid. Traditionally, researchers have modified superabsorbent polymers (SAPs) of this type by further reacting them with simple, nontoxic diols or triols such as propylene glycol or glycerine.²⁸ However, researchers at Stockhausen have found that alkylene carbonates can also be used in this application.²⁹

Table 2 shows the performance of a typical superabsorbing polymer (SAP) before and after modification with EC, PC, and BC.²⁹ In each case, alkylene carbonate, water, and ethanol (2.0 g each) were mixed with 100 g of the polymer to be modified. The mixture was then placed in an oven preheated to 215 °C and allowed to react for 15–30 min. The performance of the resulting powder was quantified by the following tests: (1) free swell capacity (FSC), the amount of saline solution (0.9% NaCl) retained by the polymer upon immersion in said liquid for 30 min; (2) absorbency against pressure (AAP), the amount of saline solution retained by the polymer upon immersion in said liquid for 1 h while under a weight exerting a force of 20 g/cm².³⁰ In both tests, the results were given in units of grams of liquid absorbed per gram of polymer. Note that, before modification, the AAP of the polymer was significantly lower than the FSC, indicating that the force of the weight squeezed out much of the absorbed liquid. However, after modification, the AAP was nearly equal to the FSC, indicating that the alkylene carbonate had reacted to create a high density of diester cross-links on the surface of the powder. These cross-links act as a hard shell, reducing the tendency of the liquid-swollen material to deform under an applied weight.

Reactions with Aliphatic Alcohols and the Synthesis of Polycarbonates

Five-membered alkylene carbonates react with aliphatic alcohols differently than with their aromatic analogues. Whereas EC reacts with phenol to yield 2-phenoxyethanol via alkylation and loss of carbon dioxide,^{15–17} EC reacts with methanol via the generalized transesterification route shown in Figure 4a. The

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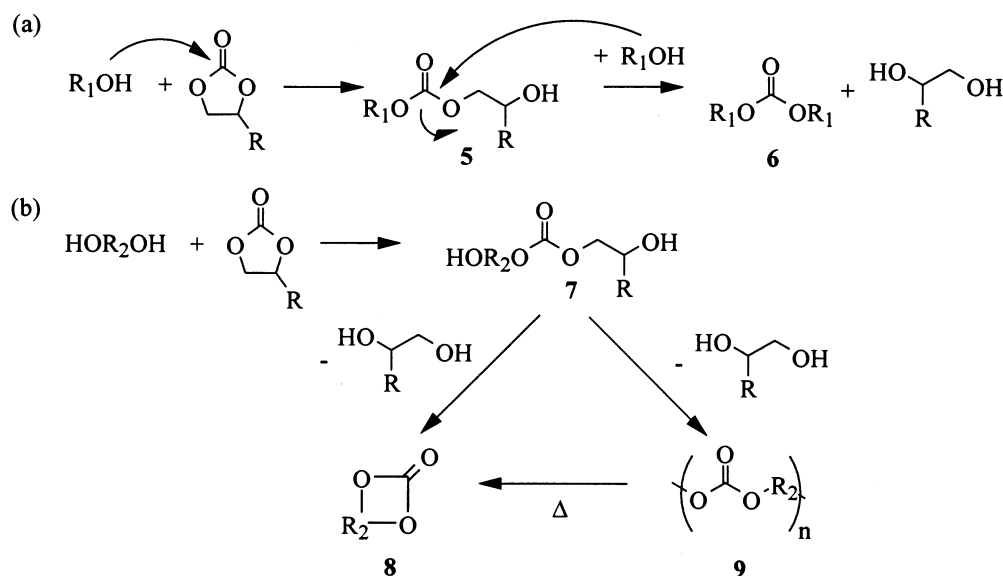


Figure 4. Reactions with aliphatic hydroxyls give dialkyl carbonates, **6**, whereas reactions with aliphatic diols give other cyclic carbonates, **8**, and/or polycarbonates, **9**. Note that there are two possible structural isomers of species **5**.

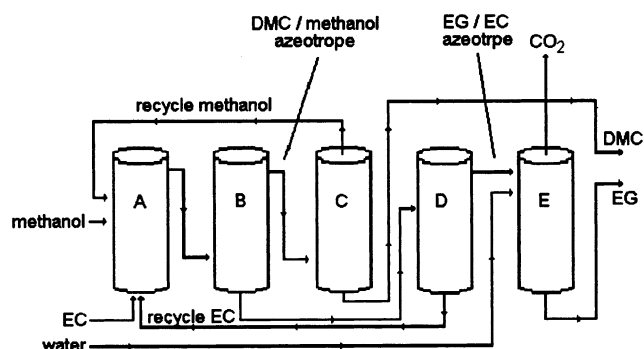


Figure 5. Process diagram for the production of DMC from EC and methanol.

Table 3. Reactions of EC with Various 1,3-Diols^a

R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	bp (°C)	yield (%)
CH ₃	CH ₃	H	H	CH ₃	H	197	39.8
CH(CH ₃) ₂	H	CH ₃	CH ₃	H	H	232	59.6
CH ₃	H	H	H	H	H	203	35.1
H	H	C ₂ H ₅	C ₄ H ₉	H	H	262	59.6
C ₃ H ₇	H	C ₂ H ₅	H	H	H	244	76.2

^a Note that reaction yield is relative to the amount of 1,3-diol used.

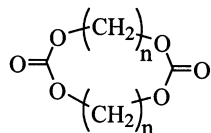
253 resulting mixture, which contains unreacted EC and
 254 methanol in addition to dimethyl carbonate (DMC) and
 255 byproduct ethylene glycol (EG), is purified by means of
 256 the process diagram shown in Figure 5.³¹ In this process,
 257 the reactants are continually fed (5:1 methanol/EC mole
 258 ratio) through a catalyst bed consisting of a weakly basic
 259 solid support catalyst such as triphenylphosphine on
 260 poly(styrene-*co*-divinylbenzene) at a temperature of 125
 261 °C and a pressure of 100 psig (reactor unit A) The
 262 resulting mixture, containing ~20% (by weight) DMC
 263 is then distilled at atmospheric pressure to remove DMC
 264 and methanol as an azeotropic mixture (reactor unit B).
 265 Methanol is then removed by distillation at 150 psig and
 266 recycled (reactor C). The purified DMC is a useful
 267 reactive intermediate in the synthesis of polycarbonate
 268 diols.

269 Five-membered alkylene carbonates can also be re-
 270 acted with diols to form other alkylene carbonates or
 271 polycarbonates, as shown in Figure 4b. In this regard,
 272 alkylene carbonates can be used in lieu of more tradi-
 273 tional reactants such as dialkyl carbonates or phos-
 274 gene.³² In such a process, the yield of alkylene carbonate
 275 produced is dependent on the boiling point difference
 276 between the reactant and byproduct diols. Researchers
 277 at Huntsman have reacted several 1,3-diols with 15%
 278 excess EC in the presence of titanium(IV)isopropoxide
 279 at 120–150 °C and 15–30 mmHg to prepare six-
 280 membered alkylene carbonates (1,3-dioxan-2-ones).³³
 281 The results are shown in Table 3. In each case, the

282 resulting six-membered alkylene carbonate (~99% pu-
 283 rity) was obtained by short-path distillation at temper-
 284 atures in the range of 150–200 °C at 1–2 mmHg. In
 285 certain cases, a mixture of cyclic carbonate and polymer
 286 was obtained. However, distillation conditions were
 287 sufficient to convert any polymer to the analogous cyclic
 288 carbonate such that only catalyst residue remained
 289 undistilled. Slight decomposition of polymer or cyclic
 290 carbonate to carbon dioxide during distillation was not
 291 taken into account. For instances in which the boiling
 292 point difference between the 1,3-diol reactant and the
 293 byproduct EG (bp = 197 °C) was small, yields of cyclic
 294 carbonate were low. This is because considerable amounts
 295 of 1,3-diol were removed from of the system along with
 296 the EG distillate.

297 Transesterification of 1,2-diols by reaction with car-
 298 bonates, cyclic or linear, gives five-membered alkylene
 299 carbonates almost exclusively. A well-known example
 300 is the reaction of dimethyl carbonate (DMC) with
 301 propylene glycol to yield PC.³⁴ In contrast, transesteri-
 302 fication of 1,X-diols, where X ≥ 4, by reaction with
 303 carbonates produces polycarbonates almost exclusively.
 304 Only when more reactive sources of carbonate are
 305 employed, such as phosgene, are seven- and higher-
 306 membered cyclic carbonates obtained in appreciable
 307 yield. For instance, Matsuo et al. reacted phosgene
 308 trimer with 1,4-butanediol at 45–50 °C and in the
 309 presence of chloroform solvent to obtain the seven-
 310 membered cyclic carbonate 1,3-dioxepan-2-one in 30%

311 yield (70% yield of polycarbonate).³⁵ In contrast, when
 312 they employed DEC in lieu of phosgene, a mere 2.7%
 313 yield of cyclic carbonate was obtained. Interestingly,
 314 further analysis of the DEC reaction product revealed
 315 that the cyclic carbonate was not the intended seven-
 316 membered ring, but the 14-membered dicarbonate ring
 317 shown below



318 in which $n = 4$.³⁵ Similar results were obtained by
 319 Kricheldorf and co-workers upon reaction of DEC with
 320 1,10-decanediol. Partial depolymerization of the product
 321 at 200–310°C followed by short-path distillation af-
 322 forded the product cyclobis(decamethylene carbonate)
 323 in 9.2% yield.³⁶

324 Given the above findings, it is not surprising that
 325 transesterification of 1,3-diols by reaction with carbon-
 326 ates, cyclic or linear, yields a mixture of cyclic carbonate
 327 monomer and polymer. Although a polycondensation
 328 mechanism is at work, ring-opening polymerization of
 329 the cyclic monomer is also likely given the reaction
 330 conditions and catalysts often employed. Therefore, it
 331 is necessary to investigate the ring-opening polymeri-
 332 zation behavior of the intended cyclic carbonate to
 333 explain the above observations. Keul and co-workers³⁷
 334 have found that the thermodynamics of alkylene car-
 335 bonate polymerization is analogous to that of lactones
 336 in that, because of increased ring strain, six- and higher-
 337 membered alkylene carbonates tend to polymerize much
 338 more readily than five-membered alkylene carbonates.
 339 This finding is consistent with that of other researchers,
 340 who have found that the analogous polymerization of
 341 five-membered alkylene carbonates such as EC and PC
 342 is often slow and plagued by side reactions that intro-
 343 duce ether linkages into the material.³⁸ This topic will
 344 be covered in more detail in a later section. In contrast,
 345 six-membered alkylene carbonates can be homopoly-
 346 merized quite easily with few, if any, ether linkages by
 347 either anionic,³⁹ cationic,^{39,40} or complexation-type⁴¹
 348 means.

349 In addition to ring size, the degree to which polymer
 350 is formed in the transesterification of 1,X-diols by
 351 reaction with alkylene carbonates also depends on the
 352 number and nature of substituents found on the cyclic
 353 carbonate product. This is most evident with regard to
 354 the synthesis of six-membered alkylene carbonates. The
 355 results of Matsuo and co-workers support this observa-
 356 tion.⁴² In their study, six-membered alkylene carbonates
 357 were synthesized from ethyl chloroformate with varying
 358 substituents at the 5-position. Each was polymerized
 359 in THF via potassium *tert*-butoxide initiator at 0 °C.
 360 After 1 h, the reaction was terminated by addition of a
 361 methanol/phosphoric acid mixture and the percent
 362 monomer conversion was determined by ¹H NMR spec-
 363 troscopy. The percent monomer conversion was found
 364 to decrease with increasing size of the substituents at
 365 R₃ and R₄. For R₃ = R₄ = CH₃, for example, a 96%
 366 conversion was observed. For R₃ = R₄ = C₆H₅, only a
 367 32% conversion of monomer was observed.

368 On the basis of the above results, particular 1,3-diols
 369 can be chosen to give polycarbonates or six-membered
 370 alkylene carbonate monomers almost exclusively. If only
 371 lightly substituted six-membered alkylene carbonates

372 such as that for which R₁ = CH₃ and R₂₋₆ = H
 373 (5-methyl-1,3-dioxan-2-one) are desired, one must de-
 374 polymerize the resulting polycarbonate in the manner
 375 detailed by Kricheldorf et al.³⁶ with the exception that
 376 most polycarbonates synthesized from 1,3-diols unzip
 377 to give the cyclic monomer under milder conditions
 378 (150–200 °C). Unlike other classes of polymers, many
 379 polycarbonates prepared from 1,3-diols can be unzipped
 380 quite easily and selectively, giving the cyclic carbonate
 381 in high yields.^{32a,43} The result is a cyclic carbonate
 382 monomer that can be repolymerized via anionic polym-
 383 erization or other ring-opening technique to give a well-
 384 defined material whose molecular weight can be con-
 385 trolled quite well. Because the polymers produced in the
 386 manner illustrated in Figure 4b typically have molec-
 387 ular weights in the range of 1000–2500,⁴⁴ the monomer
 388 must be recovered and repolymerized by means of a
 389 ring-opening technique if higher molecular weights are
 390 desired. A considerable amount of information concern-
 391 ing the synthesis of cyclic five- and six-membered
 392 alkylene carbonates and the ring-opening polymeriza-
 393 tion of such species to yield polycarbonates can be found
 394 in a recent review by Rokicki.⁴⁵

395 Because they are hydroxyl-terminated, polycarbon-
 396 ates produced by the transesterification of diols by
 397 reaction with alkylene carbonates find employment as
 398 spacers in the synthesis of polyurethanes.^{32b,46} Although
 399 polycarbonates prepared from unsubstituted diols (R₁₋₆
 400 = H) can be problematic because of poor solubility and
 401 compatibility with solvents and curing agents, this
 402 problem can be overcome by introducing alkyl- and
 403 hydroxyl-containing substituents wherein at least one
 404 of R₁₋₆ is alkyl, hydroxyl, or hydroxyalkyl.⁴⁷ The result-
 405 ant materials boast high tensile strength, flexibility, and
 406 chemical resistance. They find utility in the manufac-
 407 ture of paints, coatings, and adhesives.

Reactions with Aliphatic Amines

408
 409 As with hydroxy-functional materials, five-membered
 410 alkylene carbonates react very differently with aliphatic
 411 amines than with their aromatic analogues. They
 412 undergo attack at the carbonyl carbon atom followed
 413 by ring-opening to give a urethane (carbamate) product,
 414 **11** (Figure 6b).⁴⁸ Note that only one of two possible
 415 isomers of **11** is shown. Unlike linear carbonates (Figure
 416 6a),⁴⁹ the reaction of alkylene carbonates with amines
 417 yields a hydroxy-functional species useful as a reactive
 418 intermediate. Although similar products can be obtained
 419 via the reaction of diols with urea,⁵⁰ such reactions
 420 generally require higher temperatures (120–170 °C)
 421 and evolve ammonia as a byproduct. In addition, if
 422 hydroxyalkylurethanes are desired, care must be taken
 423 to prevent ring closure, which yields an alkylene car-
 424 bonate and a second mole of ammonia byproduct.

425 Unlike reactions that occur in the presence of ali-
 426 phatic alcohols, the hydroxyalkylurethane species pro-
 427 duced does not usually undergo further reaction with a
 428 second mole of amine to produce a urea or imidazolidi-
 429 none, except at temperatures ≥ 150 °C (Figure 6c).⁵¹
 430 For R₂ = H, cyclization of **11** yields an oxazolidinone,
 431 **12**, with loss of water. Reaction with a second mole of
 432 amine gives a hydroxyalkylurea (not shown), which also
 433 undergoes cyclization with loss of water to yield the
 434 imidazolidinone or cyclic urea, **13**. Note that this reac-
 435 tion occurs in the absence of catalyst. Should a low-
 436 boiling amine such as methylamine be employed, high
 437 pressure is required to keep the reaction mixture
 438 condensed at the necessary temperatures.

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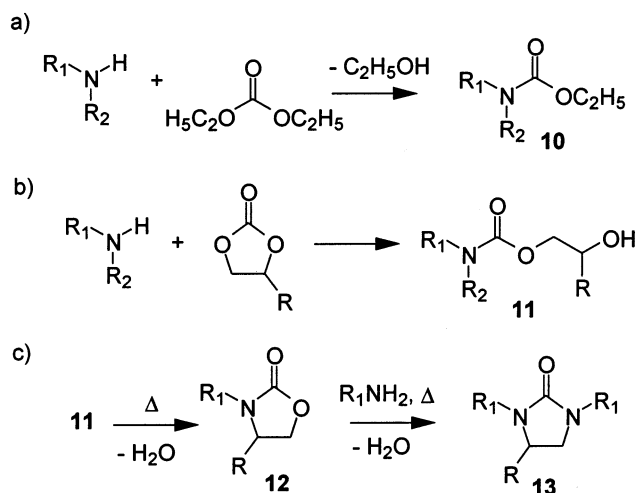


Figure 6. (a) Reaction of linear carbonates (DEC shown) with amines gives urethanes, **10**. (b) Reaction of alkylene carbonates with aliphatic amines gives hydroxylalkylurethanes, **11**. (c) Heating **11**, where $R_2 = H$, in the absence of excess amine results in cyclization and loss of water to give oxazolidinones, **12**, whereas heating in the presence of excess amine ultimately yields imidazolidinones, **13**.

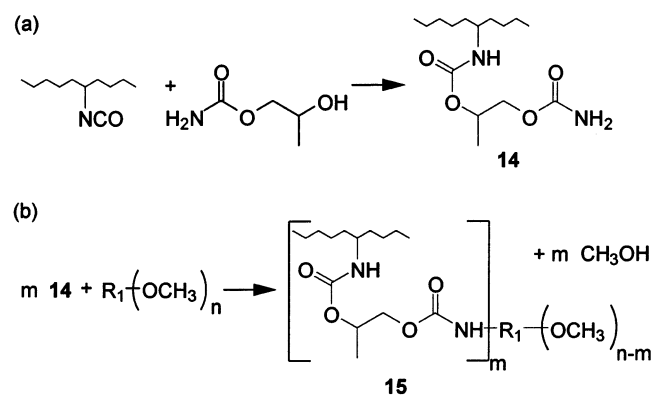
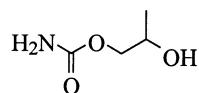


Figure 7. Synthesis of polyurethane resin for automotive coatings. (a) Reaction of HPC with isocyanate-functional polymers. (b) Reaction of carbamate-functional polymer, **14**, with cross-linking agent to give cross-linked polymer **15**.

439 Five-membered alkylene carbonates will react with
 440 primary and some secondary amines at room temper-
 441 ature. Although most reactions can be accomplished
 442 without the aid of a catalyst, alkali materials can be
 443 employed to increase the reaction rate.⁵² The reaction
 444 is accompanied by an exotherm that must be controlled
 445 by monitoring the addition rate of one component into
 446 the other.⁵³ An example is the reaction of PC with
 447 ammonia to generate hydroxypropylcarbamate (HPC)^{48a}



448 as a 50/50 ± 10% mixture of isomers (only one of which
 449 is shown). This material has found use in the automot-
 450 ive coatings industry in methods for preparing novel
 451 polyurethane resins.⁵⁴ For instance, researchers at
 452 BASF have investigated reactions of HPC with isocya-
 453 nate-functional polyacrylates to prepare carbamate-
 454 functional polymers as illustrated in Figure 7a.^{54d} The
 455 resulting products of general structure **14** were then
 456 mixed with a cross-linking agent bearing methoxy
 457 substituents such as hexamethoxymethyl melamine (*n*

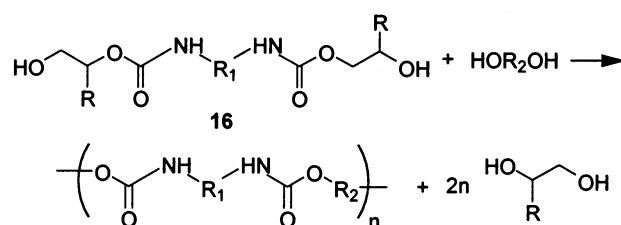
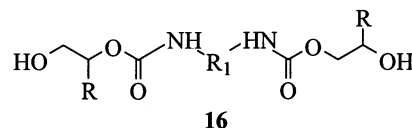


Figure 8. Reaction of a bis(hydroxyalkyl)urethane, **16**, with a polyol to produce a polyurethane.

= 6) during spray application to a surface. Subsequent
 458 baking or curing of the mixture gave urethane-cross-
 459 linked coatings, **15** (Figure 7b), in which $m = 3-4$.
 460 Although similar coatings can be obtained simply by
 461 mixing a polyisocyanate with a polyol in a spray
 462 applicator, the polyisocyanate fumes generated under
 463 such conditions can be dangerous and difficult to
 464 contain. In the above example, however, the isocyanate
 465 has been converted to the much less hazardous material
 466 **14** under controlled laboratory conditions prior to ap-
 467 plication, eliminating the dangers previously associated
 468 with this industry. The resulting coating exhibits excel-
 469 lent resistance to environmental etch (acid rain), scratch
 470 and mar, salt corrosion, and hydrolysis,⁵⁵ all necessary
 471 of coatings in the automotive industry.

472 It is well-known that polymers containing urethane
 473 linkages in their backbones can be prepared by the
 474 reaction of a diisocyanate with a polyol. However, it was
 475 discovered that the toxic diisocyanate used in this
 476 process could be replaced with the analogous diamine
 477 with the assistance of alkylene carbonates. Researchers
 478 at King Industries reacted alkylene carbonates with
 479 aliphatic diamines to give difunctional hydroxyalkyl
 480 urethanes of structure **16**
 481



482 which act as blocked isocyanates.⁵⁶ **16** was then reacted
 483 with a polyester polyol in the presence of a tin tran-
 484 s-esterification catalyst at 160 °C to produce the desired
 485 polyurethane with removal of the byproduct glycol by
 486 distillation (Figure 8). Thus, a polyurethane was pre-
 487 pared without the need for isocyanates.

488 In addition to polyurethanes, the above technology
 489 has also been applied to the modification of amino acids
 490 for the production of biocompatible polymers⁵⁷ and
 491 dispersants for use in lubricating oils, hydraulic oils,
 492 and gasoline. For instance, researchers at Chevron have
 493 capped polyisobutylene with maleic anhydride followed
 494 by reaction with ethylene amines such as triethylene
 495 tetraamine (TETA) to form polyalkylene succinimides.
 496 They have found that reaction of EC with the resulting
 497 secondary and primary amines yields hydroxyalkylure-
 498 thane adducts with superior dispersant characteristics
 499 (Figure 9).⁵⁸ These adducts are useful in reducing engine
 500 deposits such as sludge and ash resulting from incom-
 501 plete combustion. Modification via ethylene carbonate
 502 also improves the compatibility of the polyalkylene
 503 succinimide dispersant with other components of the
 504 formulation.

505 Alkylene carbonates can also be reacted with amines
 506 that contain hydroxyl groups to give added functionality
 507 to the urethane product. However, reactions with β-hy-

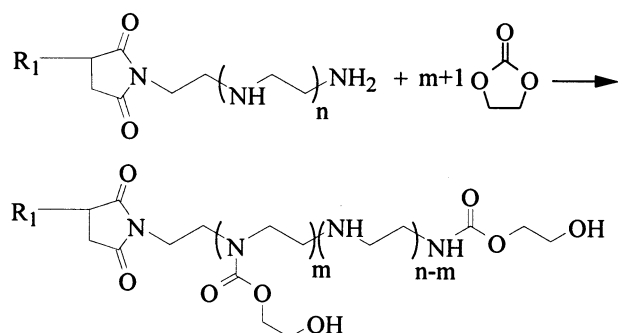


Figure 9. Modification of polyalkylenesuccinimide dispersants by reaction with EC, $n = 3-5$, $m = 1, 2$. $R_1 =$ polyisobutylene backbone.

droxyalkylamines such as ethanolamine are often accompanied by cyclization and loss of glycol to give oxazolidinones under mild heating (Figure 10).⁵⁹ Oxazolidin-2-one ($R_1 = H$) in particular can also be prepared by the reaction of EC with urea.⁶⁰ Such materials and their derivatives find use as medicinal actives for the treatment of bacterial infections, arthritis, and toxicity caused by chemotherapy.⁶¹

Although the bulk of this section, and indeed most of this review, has focused on the reactive applications of five-membered alkylene carbonates, EC and PC in particular, it should be noted that six-membered cyclic carbonates (1,3-dioxan-2-ones) can also be reacted with aliphatic amines.⁶² Tomita et al. have reacted allyl-functional five- and six-membered alkylene carbonates with n -hexylamine and benzylamine in the absence of catalyst at various temperatures to compare their reactivities.^{62a} By monitoring the carbonate conversion by ¹H NMR spectroscopy and assuming second-order kinetics, they determined that the rate constant ratio, $k' = k_1/k_2$, where k_1 and k_2 are the rate constants for the reaction of six- and five-membered alkylene carbonates, respectively, is 28–60 depending on the reaction temperature and amine employed. Thus, the 1,3-dioxan-2-ones react much more quickly with amines than do the corresponding 1,3-dioxolan-2-ones, reaching completion in shorter times and at lower temperatures. Should such materials become available commercially, they might even be viable in spray coating applications for large surfaces, such as airport terminal flooring, which must cure quickly and at ambient temperatures.

Ring-Opening Polymerization of Alkylene Carbonates

As stated earlier, five-membered alkylene carbonates undergo ring-opening polymerization with difficulty. Soga and co-workers were among the first researchers to report this behavior.³⁸ In fact, the ceiling temperature, t_c , for the process is quite low. For instance, a t_c of only 25 °C was reported for the ring-opening polymerization of EC.⁶³ Nevertheless, EC and other 1,3-dioxolan-2-ones have been polymerized at temperatures exceeding 100 °C. To understand this apparent inconsistency, it must be noted that polymerization involves loss of carbon dioxide such that the polymer produced contains both carbonate and ether linkages.

It has recently been proposed that the anionic ring-opening polymerization of EC takes place according to the mechanism illustrated in Figure 11.^{63,66} Following initiation (Figure 11a), the propagating chain can add EC via attack at the carbonyl (Figure 11b) or alkylene

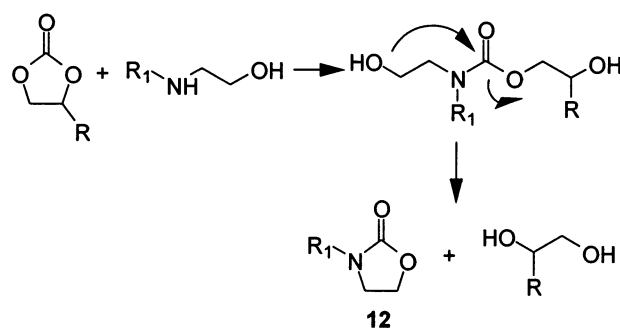


Figure 10. β -Hydroxyalkylamines often undergo cyclization to oxazolidinones, **12**, prior to reaction with alkylene carbonates.

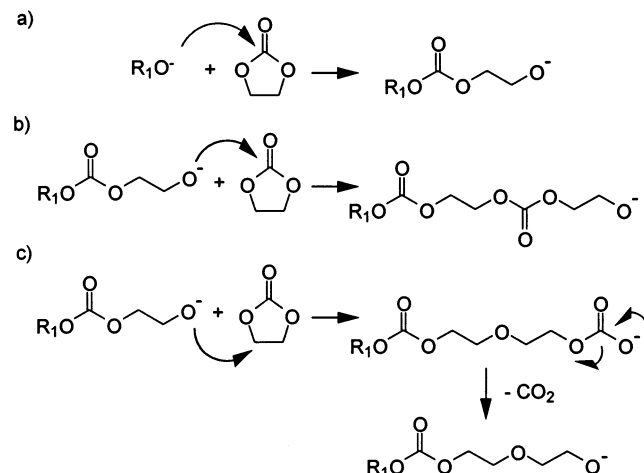


Figure 11. (a) EC ring-opening initiated by an anionic species. (b) Propagation via carbonyl attack, yielding a carbonate linkage. (c) Propagation via alkylene attack, yielding an ether linkage and loss of carbon dioxide.

(Figure 11c) carbon, resulting in the production of a carbonate or ether linkage, respectively. Assuming that ΔS of decarboxylation is positive,⁶³ polymerization of 1,3-dioxolan-2-ones at temperatures above t_c for traditional ring-opening does not violate thermodynamic principles. However, data generated by Vogdanis et al.⁶⁴ reveal that the polymerization process is somewhat different from that illustrated in Figure 11. Recognizing that the entropy of ring-opening polymerization, ΔS_p , is positive and using the well-known relation

$$\Delta G_p = \Delta H_p - T\Delta S_p$$

it can be said that, for the process to occur spontaneously ($\Delta G_p < 0$), the enthalpy of ring-opening polymerization, ΔH_p , must be negative. This was not found to be the case, as ΔH_p values of 124.6, 125.6, and 112.5 kJ/mol were measured for the ring-opening polymerization of EC, resulting in pure poly(ethylene carbonate), at temperatures of -73 , 25, and 170 °C, respectively. Thus, the reaction scheme illustrated in Figure 11b is not possible according to thermodynamic principles.

Alternatively, Vogdanis and co-workers⁶⁵ proposed that the carboxylate ion produced via the scheme illustrated in Figure 11c can add an additional molecule of EC as well as undergo decarboxylation. Note that this is very different from the mechanism given in Figure 11, for which Lee and co-workers⁶³ claim that the alkylate ion generated as a result of decarboxylation, rather than the carboxylate ion, is the active chain-propagating species. For the thermodynamic reasons discussed above, Vogdanis and co-workers state that

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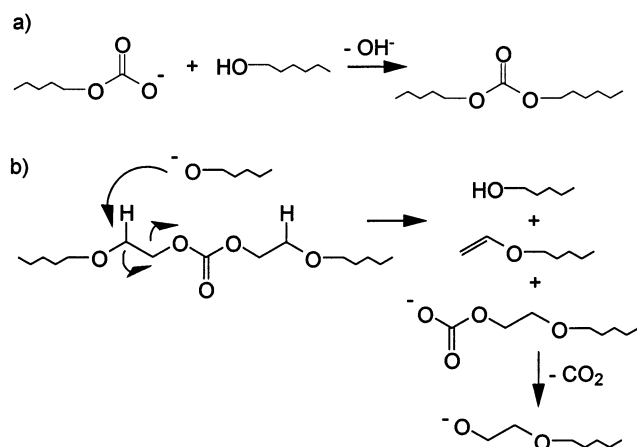
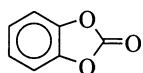


Figure 12. (a) Reaction of carboxylate ion with the hydroxy terminus of another polymer chain. (b) Mechanism proposed by Lee et al.⁶³ for stage two polymer degradation.

only one carbonate linkage can be formed in the aforementioned manner before decarboxylation and subsequent ether linkage formation. Thus, the fraction of carbonate linkages in the polymer relative to ether linkages cannot exceed 50%. It should also be noted that evidence suggests that the carboxylate ion shown in Figure 11c can react with the hydroxy terminus of another polymer chain, connecting two chains through a carbonate linkage (Figure 12a).⁶⁶ At this time, it should be reiterated that, if polymerization is initiated by an aromatic species such as the phenolate ion,⁶⁷ then initiation involves CO₂ loss exclusively, in keeping with the method of alkylene carbonate alkylation discussed earlier (Figure 2).

Interestingly, Lee and co-workers have studied the polymerization of EC initiated by KOH at various temperatures (150–200 °C) and ratios of carbonate to initiator (1000:1 to 20:1) and discovered that the reaction can be described as a two-stage process. In this manner, the final polymer obtained is the result of not only initiation and propagation but also chain cleavage.⁶³ In the first stage, the molecular weight of the polymer increases with reaction time to a maximum molecular weight in the range of 1000–9000 depending on the carbonate-to-initiator ratio employed. The material generally has a carbonate-to-ether linkage ratio of about 2 (30–32% carbonate), which remains fairly constant until approximately 90–100% monomer conversion. In the second stage, the molecular weight and carbonate content of the material decrease significantly with continued heating. In addition, the presence of a vinyl moiety can be seen by NMR analysis. To account for these observations, they proposed the chain cleavage mechanism shown in Figure 12b.

As seen with six-membered cyclic carbonates, polymerization of 1,3-dioxolan-2-ones is dependent on the number and size of substituents on the carbonate ring. Whereas EC and PC can be polymerized to molecular weights of >50 000, the highly substituted benzo-1,3-dioxolan-2-one



does not polymerize at all.⁶⁸

It is widely recognized that the preferred method of producing poly(alkylene oxide-co-alkylene carbonate)s

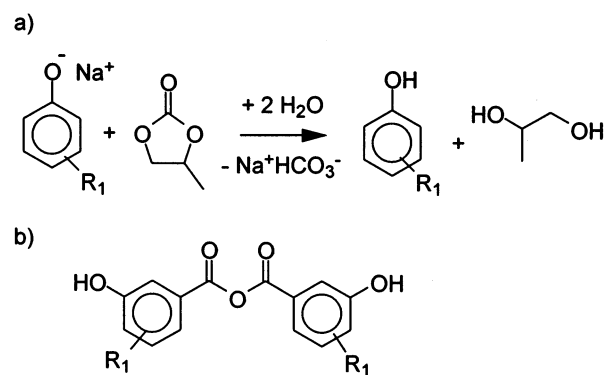


Figure 13. (a) Proposed mechanism of PF cure acceleration via PC hydrolysis. (b) Cross-linking structure detected by Pizzi et al.^{77a} R₁ represents the remainder of the PF resin.

is via the copolymerization of the desired alkylene oxide, for instance, ethylene oxide (EO), and CO₂. Both academic and industrial researchers have studied this type of reaction in detail. Typically, the reaction is performed within the temperature range 75–150 °C under pressures of 100–500 psi. Useful initiators for the process include zinc(II)phenoxides,⁶⁹ zinc dicarboxylates,⁷⁰ β-diminate zinc complexes,⁷¹ stannate salts,⁷² diethylzinc,⁷³ and triethylaluminum,⁷³ to name but a few. A more complete listing is presented in a review by Darenbourg et al.⁷⁴ The resulting materials have found utility as nonionic surfactants,⁷² binders for glass and ceramics,⁷⁵ and as possible cosolvents for use in supercritical CO₂ applications.⁷⁶ However, the molecular weight of such materials is often difficult to control. Although it is debatable whether polymerization of the five-membered cyclic carbonates offers better molecular weight control, such processes do offer a low-pressure alternative to those not able or willing to employ the pressures required of alkylene oxide/CO₂ copolymerization.

Unlike the 1,3-dioxolan-2-ones, six- and seven-membered alkylene carbonates polymerize much more rapidly and selectively. The details of such polymerizations are described in a previous section.

Alkylene Carbonates as Cure Accelerators

In addition to their utility as chemical intermediates, alkylene carbonates also find use as cure accelerators of phenol–formaldehyde (PF)⁷⁷ and sodium silicate (SS)⁷⁸ resin systems, which are widely used in foundry sand and wood binder applications. Although the effect of alkylene carbonates, particularly PC, on the reaction of phenol and formaldehyde in the presence of sodium hydroxide has been studied for some time, the exact mechanism responsible for cure acceleration is still a subject of debate. Unfortunately, analysis of cured PF resins has been hampered by the fact that such materials contain numerous isomers and are only sparingly soluble. Tohmura and co-workers^{77c} claim that propylene carbonate is quickly hydrolyzed to propylene glycol and sodium hydrogen carbonate (Figure 13b) when exposed to the conditions required for PF cure. Thus, it is the sodium hydrogen carbonate byproduct, a cure accelerator in its own right, that is responsible for the accelerated cure. Although Pizzi et al. agrees that PC hydrolysis does occur to some extent, they propose mechanisms in which the cyclic carbonate actively participates in bridging reactions.^{77a} On the basis of ¹³C NMR observations, they claim the existence of anhydride bridges (Figure 13b) not found when sodium

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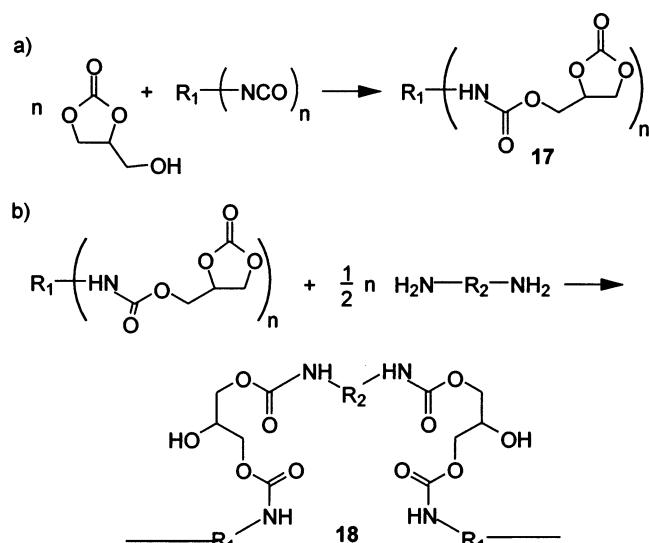
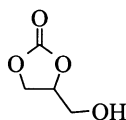


Figure 14. Reaction of GC with an n -functional isocyanate creates an n -functional alkylene carbonate, **17**. Reaction of **17** with a diamine gives a useful polyurethane resin, **18**. Note that **18** can be linear ($n = 2$) or a network ($n > 2$).

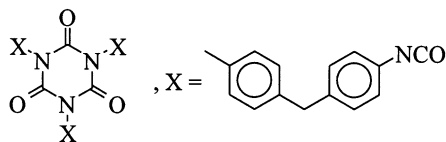
hydrogen carbonate alone is employed as an accelerant.^{77d} A few observations made by Park and co-workers^{77e} seem to support this idea; however, they concede that more conclusive evidence is needed. It might be possible that both mechanisms are at work.

Five-Membered Alkylene Carbonates that Include Added Functionality

No review of this nature would be complete without a brief discussion of alkylene carbonate derivatives aside from the simple alkyl-substituted cyclics. With this in mind, many derivatives of **1** have been developed in recent years that contain added functionality, that is, 1,3-dioxolan-2-one derivatives that contain reactive groups in addition to the carbonate ring itself. Examples include vinyl moieties, esters, ethers, and alcohols. Of these, only glycerol (glycerin) carbonate (GC)



is available commercially. The material can be synthesized by the reaction of glycerin with a carbonate source such as phosgene, a dialkyl carbonate,⁷⁹ or an alkylene carbonate;⁸⁰ by reaction of glycerin with urea,⁸¹ carbon dioxide, and oxygen;⁸² or by reaction of carbon dioxide with glycidol. Because it contains a hydroxy-functional substituent, GC can be reacted with anhydrides,⁸³ acyl chlorides,^{79a} isocyanates,⁸⁴ and the like. For instance, researchers at Imperial Chemical Industries reacted GC with the multifunctional isocyanate polymeric MDI



in the presence of potassium acetate to create a multifunctional alkylene carbonate of the general structure **17**, shown in Figure 14a.^{84a} The reaction of GC with

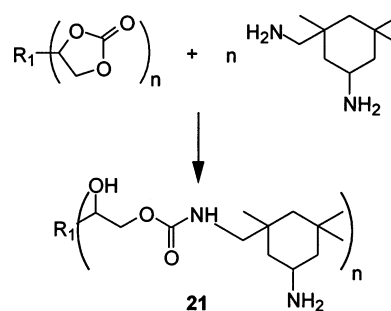
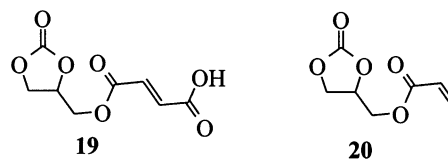


Figure 15. Reaction of multifunctional alkylene carbonates with IPDA to produce an amine-functional cross-linking agent, **21**. Note that only one structural isomer of **21** is shown.

isocyanates occurs at room temperature or with slight heating and is generally accompanied by an exotherm such that the controlled addition of one component into the other is desired. By monitoring for the presence of isocyanate by IR spectroscopy, the necessary reaction time can easily be determined.

The multifunctional carbonates prepared by means of the above process are useful as blow promoters in the preparation of polymeric foams,^{84a} or they can be reacted with aliphatic diamines to prepare polyurethane resins, **18** (Figure 14b).⁸⁵ Although specific details concerning the reaction of alkylene carbonates with amines were discussed in a previous section, it should again be noted that a promoter is not required and that a temperature increase, sometimes as much as $\Delta t = 75^\circ\text{C}$, is observed upon mixing. The components can be mixed in the presence of a polar solvent such as DMF with stirring until a high viscosity is obtained. Once cured at $50\text{--}75^\circ\text{C}$ for 12–48 h, the resulting resins can be readily cast into films with excellent clarity and tear resistance or extruded into fibers having high tensile strengths.^{85a}

Vinyl-functional alkylene carbonates, useful in the preparation of polymers that contain alkylene carbonate pendant groups, can also be prepared from GC. Two examples are the reaction of GC with maleic anhydride and acrylyl chloride to produce the acrylate-functional cyclic carbonates **19** and **20**, respectively.^{83a}



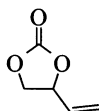
Although the transesterification of alkyl esters such as dimethyl maleate or methyl acrylate by reaction with GC represents an obvious means of obtaining the above materials, the temperatures required of such processes ($>100^\circ\text{C}$) result in unwanted polymerization of both the reactant and product species, even in the presence of well-known radical inhibitors such as 2,6-di-*tert*-butyl-*p*-cresol.^{83a} In addition, the synthesis of vinyl-functional alkylene carbonates such as **19** and **20** is greatly complicated by the fact that such materials cannot be purified by distillation and must be stored at temperatures $< 0^\circ\text{C}$.^{86,87} In fact, these and similar species are known to undergo polymerization much more readily than the analogous underivatized vinyl monomers.⁸⁸

Despite the synthetic challenges, the novel polymers produced from the above monomers can be modified for use in a wide range of applications by reacting the alkylene carbonate pendant moieties employing any of the synthetic techniques described above. For instance,

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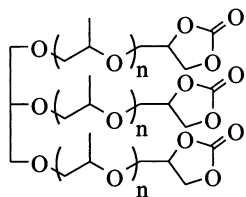
754 several researchers have documented the reaction of
755 alkylene carbonate-containing polymers with amines
756 and diamines to produce graft and network poly-
757 mers.^{87,88b,89}

758 Vinyl-functional alkylene carbonates can also be
759 prepared from the corresponding epoxides in a manner
760 similar to the commercial manufacture of EC and PC
761 via CO₂ insertion.¹ The most notable example of this
762 technology is the synthesis of 4-vinyl-1,3-dioxolan-2-one
763 or vinyl ethylene carbonate (VEC) from 3,4-epoxy-1-
764 butene.



765 Originally reported by Bissinger and co-workers in
766 1947⁹⁰ and later by DuPont,⁹¹ much of the latest
767 research involving this molecule has been performed by
768 Webster and Crain at Eastman. Preliminary studies
769 have found that VEC can be copolymerized with readily
770 available vinyl monomers useful in the coatings indus-
771 try, such as styrene, alkyl acrylates and methacrylates,
772 and vinyl esters.⁹² With the exception of styrene, the
773 authors found that VEC will undergo free-radical solu-
774 tion or emulsion copolymerization, although not quan-
775 titatively, with all comonomers studied to produce
776 polymeric species with a pendant five-membered alky-
777 lene carbonate functionality that can be further cross-
778 linked by reaction with amines.⁹³ A more complete
779 review of vinyl-functional five-membered alkylene car-
780 bonates and their potential in the manufacture of novel
781 cross-linkable polymers has been provided by Webster
782 and Crain.⁹⁴

783 Although not yet commercially available, multi-alky-
784 lene carbonates can also be prepared from epoxy resins
785 via CO₂ insertion.^{54c,95} An example is the insertion of 3
786 mol of CO₂ into Heloxy Modifier 84 (Shell), a trifunc-
787 tional epoxy-terminated polyoxypropylene based on
788 glycerine. The result is the trifunctional alkylene car-
789 bonate shown below



790 where $n \approx 8$. As with other cyclic carbonates, these and
791 similar materials can be further reacted with amines
792 to yield novel polyurethanes.^{95b-d} The extensive body
793 of research performed by Endo and co-workers in this
794 area has led to a much greater understanding of the
795 chemistry involved, thereby allowing its emergence in
796 industry. For example, researchers at Fiber-Cote have
797 reacted this material with isophorone diamine (IPDA)
798 to prepare the amine-functional adduct shown in Figure
799 15a.^{54c} The reaction takes advantage of the significant
800 difference in the reactivity of the aliphatic amine versus
801 the cycloaliphatic amine with alkylene carbonates such
802 that only the aliphatic amine participates in reaction.
803 The result is an adduct that can be reacted with epoxy
804 resins to form useful urethane coatings without the need
805 for isocyanates.

Future Outlook

The reactive applications of alkylene carbonates is
exhaustive. As new applications continue to be devel-
oped regarding commercially available alkylene carbon-
ates, the demand for carbonate-functional cross-linkable
polymers, polycarbonates, and other functional deriva-
tives such as those discussed in previous sections is on
the rise. Large-scale production of these novel sub-
stances such that they can be made available at reason-
able costs is the challenge that faces future researchers
in this field.

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