

· 综述 ·

基于二氧化碳/二醇反应环碳酸酯的合成与开环聚合

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摘 要 二氧化碳(CO₂)转化为高附加值精细化学品和高分子材料,已成为高分子化学和绿色化学等领域的研究热点.其中,CO₂与二醇反应合成环碳酸酯是重要的方向之一,通过环碳酸酯的催化可控开环聚合可以制备不同结构和性能的聚碳酸酯材料.本综述以1,3-二醇衍生物、1,4-二醇衍生物、1,5-二醇衍生物与CO₂反应分类,介绍了六元环、七元环和八元环碳酸酯单体的合成与开环聚合研究进展,并且对相关领域所面临的机遇与挑战进行了探讨和展望.

关键词 二氧化碳;二醇;环碳酸酯;开环聚合;聚碳酸酯

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在碳达峰、碳中和国家战略背景下,二氧化碳(CO₂)减排与高值化利用已成为化学、化工、材料、环境等领域共同关注的重大课题^[1~10].作为一种廉价、无毒、丰富且可再生的碳源,CO₂的催化转化技术近年来取得了显著进展,主要包括热催化转化法^[11,12]、电催化转化法^[13~16]、光催化转化法^[17~20]和生物转化法^[21,22]等,成功转化为碳氢化合物^[23,24]、醇^[25,26]、羧酸衍生物^[27~29]、尿素^[30,31]和碳酸酯^[32~34]等(图1(a)).其中,环碳酸酯是一类极具应用价值的CO₂基化合物,不仅可用作绿色溶剂和锂电池电解液,还可作为单体经开环聚合(ROP)制备结构可控、性能可调的脂肪族聚碳酸酯新材料,为发展可持续高分子材料提供了路径^[35~40].根据环的大小,可分为五元环、六元环、七元环、八元环和大环碳酸酯.五元环因环张力较小,难以通过开环聚合制备聚碳酸酯,主要用于溶剂、电解质以及和胺反应制备非异氰酸

酯聚氨酯^[41~45].值得注意的是,当五元环碳酸酯具有反式稠合或双环等刚性并环结构时,环张力显著增加,可在温和条件下实现开环聚合^[46~48].六元环及以上的中、大环碳酸酯则因具有足够的环张力,可作为单体经开环聚合制备结构可控的聚碳酸酯^[37,38].对于环尺寸更大的大环碳酸酯(通常≥十二元环),1,5,7-三氮杂双环[4.4.0]癸-5-烯(TBD)、脂肪酶等可以催化进行开环聚合^[49,50].环碳酸酯开环聚合主要取决于环张力、取代基结构以及催化体系等综合因素^[51~55].

脂肪族聚碳酸酯具有良好的生物降解性、生物相容性,广泛应用于生物医学、电子材料、可持续材料等方面^[56~58].目前,脂肪族聚碳酸酯的合成方法主要包括:直接缩聚法(CO₂或碳酸二甲酯与二醇)、开环共聚法(CO₂与环氧化物)以及开环聚合(CO₂与二醇合成环碳酸酯作为单体)(图1(b)).直接缩聚法操作简单、原料易得,但通

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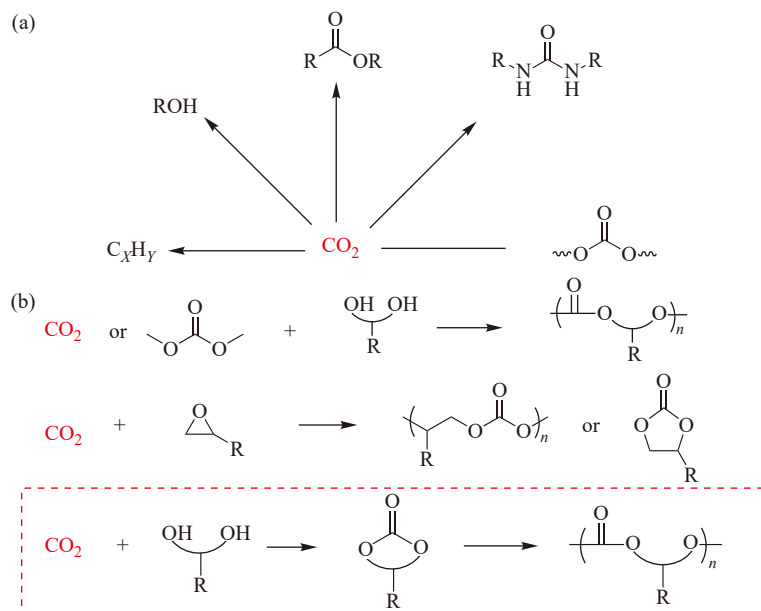


Fig. 1 (a) CO₂ conversion into various high-value chemicals; (b) Synthetic routes to aliphatic polycarbonates.

常需要高温、高真空等苛刻条件，分子量控制困难^[59-61]；开环共聚法原子经济性高、聚合可控性好，对催化剂的要求较高^[62-65]；开环聚合具有反应条件温和、聚合产物结构可控等优势^[66-68]，部分体系可以实现“单体—聚合物—单体”闭环化学回收，成为高分子合成化学和绿色化学等领域研究热点^[69,70]。

本综述聚焦基于二氧化碳/二醇反应环碳酸酯的合成与开环聚合。根据二醇的碳链长度，(含有取代基的)1,3-二醇、1,4-二醇和1,5-二醇可分别构建六元环、七元环、八元环碳酸酯(图2)。通过发展高效催化体系，实现环碳酸酯可控开环聚合，制备不同结构和性能的脂肪族聚碳酸酯。希望对二氧化碳利用和聚碳酸酯合成等相关领域提供借鉴。

1 六元环碳酸酯的合成与开环聚合

与五元环碳酸酯相比，六元环碳酸酯具有更大的环张力，进行开环聚合在热力学上更为有利，易于实现可控聚合^[71,72]。本节将介绍以糖类衍生物、木质素衍生物、甘油衍生物、丙酸酯衍生物和聚羟基脂肪酸酯回收衍生物1,3-二醇为原料，设计构建六元环碳酸酯单体，总结这些单体开环聚合的基本规律以及产物聚碳酸酯的相关性能。

1.1 糖类衍生物 1,3-二醇

糖类单体及聚合物具有良好的生物相容性、生

物降解性、结构多样性和后修饰性^[73,74]。Buchard等^[75]以D-甘露糖和CO₂为原料，合成了六元环碳酸酯单体。通过有机催化区域选择性可控聚合，得到了高玻璃化转变温度(*T_g*)的可降解糖基聚碳酸酯(图3(a))。以前期报道的温和“两步法”策略^[76]，以构型确定的1-O-甲基-α-D-甘露糖为原料，首先进行2,3-位羟基的异丙叉保护，随后在DBU存在下实现常压CO₂的插入，再经对甲苯磺酰氯(TsCl)驱动分子内环化，最终以57%的分离产率获得了目标单体。该路线条件温和、原子经济性高，完整保留了糖环的手性。同时，异丙叉保护基的引入为后续功能化提供了位点。以有机碱TBD为催化剂，室温下实现了高度区域选择性可控聚合，分子量随转化率线性增长，所得糖基聚碳酸酯数均分子量可达23.6 kDa，同时分子量分布较窄(分散度*D*=1.17)。密度泛函理论(DFT)计算表明，2,3-位异丙叉保护基产生的空间位阻引导反应优先发生于位阻较小位点，形成以“头-尾”连接为主的区域规整聚合物(88%) (图3(b))。聚合后通过酸处理选择性脱除异丙叉保护基，暴露出邻二醇活性位点，为材料的后功能化提供了便利。产物糖基聚碳酸酯的玻璃化转变温度*T_g*达到152 °C，这主要归因于刚性糖环结构单元、大体积异丙叉侧基对链运动的限制以及规整主链的协同作用。这样的无定形材料兼具高热性能与可控降解特性，在高性能可持续塑料、骨组织工程支架、药物控释载体等领域具有应用潜力。

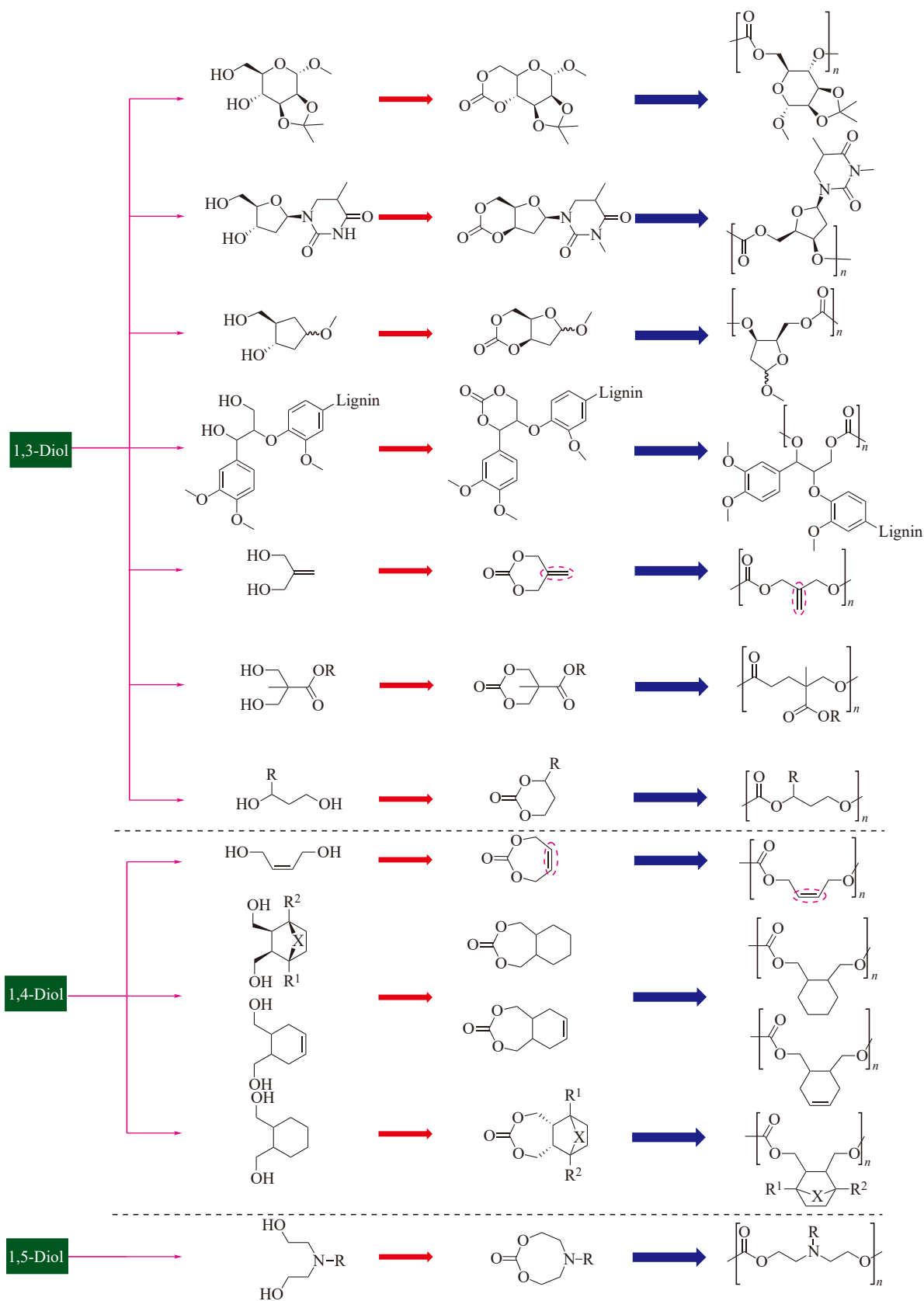


Fig. 2 Synthesis and ring-opening polymerizations of cyclic carbonates derived from CO_2 /diol reactions.

胸苷基环碳酸酯的合成长期面临挑战，聚合产物分子量较低^[77]。Buchard等^[78]利用常压 CO_2 驱

动胸苷发生立体化学翻转，成功合成出顺式稠合环状碳酸酯单体。单体合成中，胸苷的胸腺嘧啶

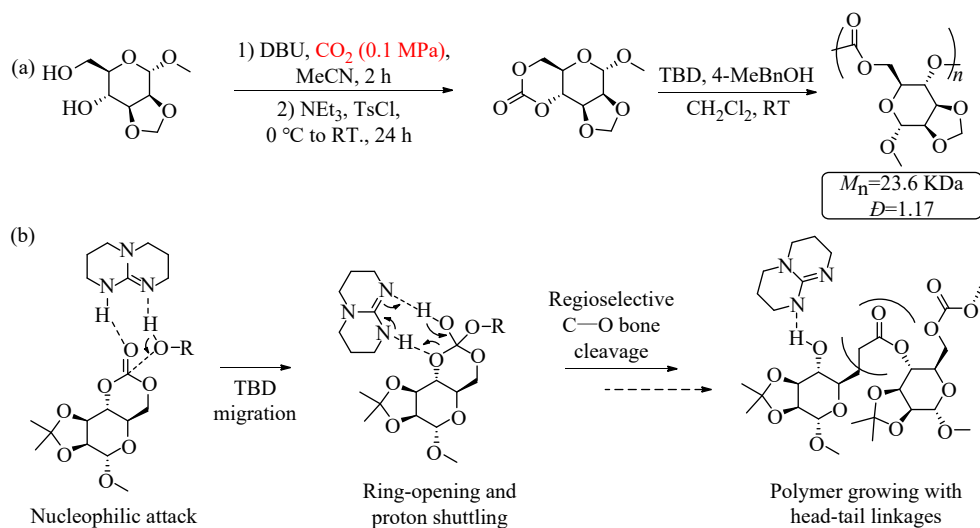


Fig. 3 (a) *D*-mannose cyclization under 1 atm CO₂ protection and TBD-catalyzed organocatalytic ring-opening polymerization using 4-methylbenzyl alcohol as an initiator; (b) The region-selective ring-opening polymerization mechanism leads to regional regularity.

碱基 *N*-3 位预先甲基化保护以抑制副反应, 同时对 3'-羟基进行选择性的甲苯磺酰化. 随后, 在 DBU 存在下将常压 CO₂ 插入 5'-羟基生成氨基甲酸酯中间体. 中间体通过 SN2 型反应取代 3'-位甲苯磺酰基, 导致碳原子构型反转, 以 52% 的产率得

到顺式耦合环状碳酸酯单体(图 4(a)). 单晶结构证实了顺式耦合构型与立体反转, 呋喃糖环呈现扭曲构象. 采用有机碱 TBD 催化剂、4-甲基苄醇引发剂, 实现了可控开环聚合, 产物分散度较低($D \approx 1.12 \sim 1.30$), 数均分子量可达 1.7 kDa (图 4(b)). 值

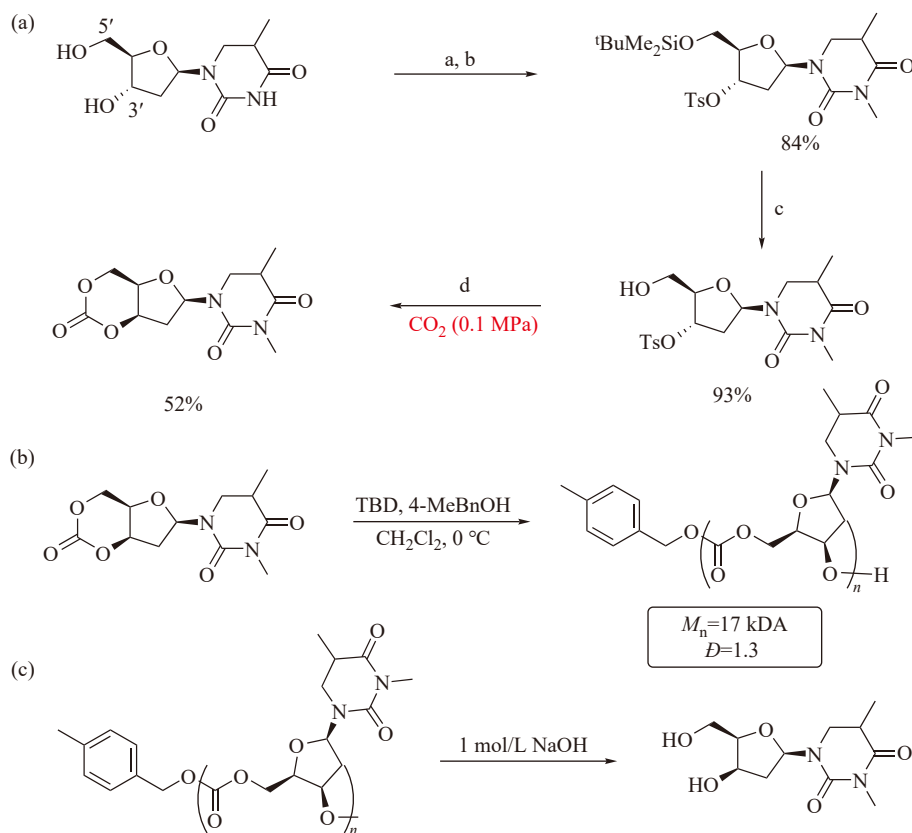


Fig. 4 (a) Synthesis of cyclic carbonate; (b) Organocatalytic ring-opening polymerizations by TBD with 4-methylbenzyl alcohol as initiator; (c) Depolymerization of thymidine cyclic carbonate under 1 mol/L NaOH conditions.

得注意的是, 聚合体系具有热力学平衡特征: 升温至 80 °C 可实现聚合物近乎定量解聚, 高效回收初始单体, 实现了“化学闭环循环”. 所得胸苷基聚碳酸酯展现出 156 °C 的极高 T_g , 这源于刚性呋喃糖骨架与胸腺嘧啶侧基的协同作用. 此外, 该聚合物在碱性条件下可完全水解(图 4(c)).

Buchard 等^[79]将天然糖 2-脱氧-D-核糖转化为六元环状碳酸酯单体, 研究了开环聚合及与三甲基碳酸酯(TMC)开环共聚的行为(图 5). 针对游离 2-脱氧核糖主要以吡喃糖形式存在的难题, 通

过将异头羟基甲基化实现了对呋喃糖形式的“动力学捕获”, 随后经选择性保护、活化及 CO_2 插入与分子内环化, 构建了顺式耦合单体, 分离得到 α 与 β 2 种端基异构体. 采用 TBD 催化, 环张力更高的 α -异构体可进行可控均聚, 但均聚物溶解性极差; β -异构体则无法均聚. 两者均可与 TMC 高效共聚, 通过调节投料比可精确控制共聚物组成, 获得数均分子量高达 64 kDa 的无规共聚物. 共聚物的 T_g 随糖单元含量增加而线性升高, 可在 -25~58 °C 的宽范围内精准调控.

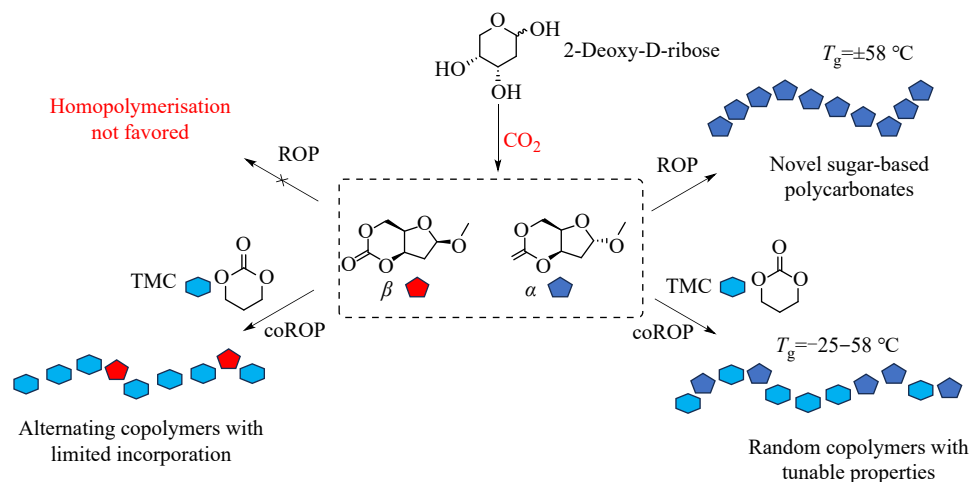


Fig. 5 CO_2 and natural sugar 2-deoxy-D-ribose were used to prepare two types of substituted sugar cyclic carbonate monomers, as well as their ring-opening polymerization and copolymerization with trimethylene carbonate to prepare aliphatic polycarbonates with tunable properties.

金属-*N*-杂环卡宾(M-NHC)配合物是一类高性能催化剂^[80]. Lamberti 等^[81]开发了一类基于 *N*-杂环卡宾(NHC)的锌配合物, 用于催化六元环碳酸酯开环聚合. 采用 Buchard 等^[82]报道的“一锅一步法”策略, 以糖发酵的生物基 1,3-二醇为原料, 在常压 CO_2 和室温条件下, 以 TsCl 和 2,4,6-三甲基吡啶(TMP)为温和碱, 合成了环状碳酸酯单体, 如 4-甲基-1,3-二氧杂环己烷-2-酮(Me-TMC)和 1,3-二氧杂环己烷-2-酮(DTC), 产率 70%~75%. 该锌配合物在醇引发剂存在下表现出优异的开环聚合催化活性. 机理研究表明(图 6(a)), 锌配合物与醇先形成加合物, 原位释放活性催化物种, 通过配位-插入机制实现链增长, 开环优先发生在位阻较小的亚甲基碳上, 形成以“头-尾”连接为主的规整结构(图 6(b)). 通过使用不同结构的醇引发剂, 可精确调控聚合物端基, 获得遥爪聚合物和嵌段共聚物.

1.2 木质素衍生物 1,3-二醇

木质素是储量第二大的天然高分子, 木质素的高芳香族结构赋予材料优异的强度、刚性和热稳定性^[83~86]. Chung 等^[87]合成了一种基于 CO_2 与木质素的全生物基可闭环化学回收的聚碳酸酯. 采用 Buchard 等^[76]报道的温和的“两步法”策略, 以 64% 的产率获得环状碳酸酯单体. 结构表征证实, 木质素结构中 β -O-4 单元的 α -和 γ -羟基被成功转化为环碳酸酯, 而部分 γ -羟基得以保留, 这些残留羟基在后续聚合中充当了“内置引发剂”, 无需外加引发剂(图 7(a)). 在无需外加醇引发剂的条件下, 利用单体自身残留羟基引发, 实现了室温下的可控聚合. 通过调节催化剂种类、用量和反应时间, 可有效控制聚合过程. TBD 的催化效率显著优于 DBU, 归因于 TBD 更强的碱性及双功能催化特性. 在 1% TBD 作用下反应 30 min, 可获得高分子量聚碳酸酯($M_n=154.58$ kDa, $D=1.48$)

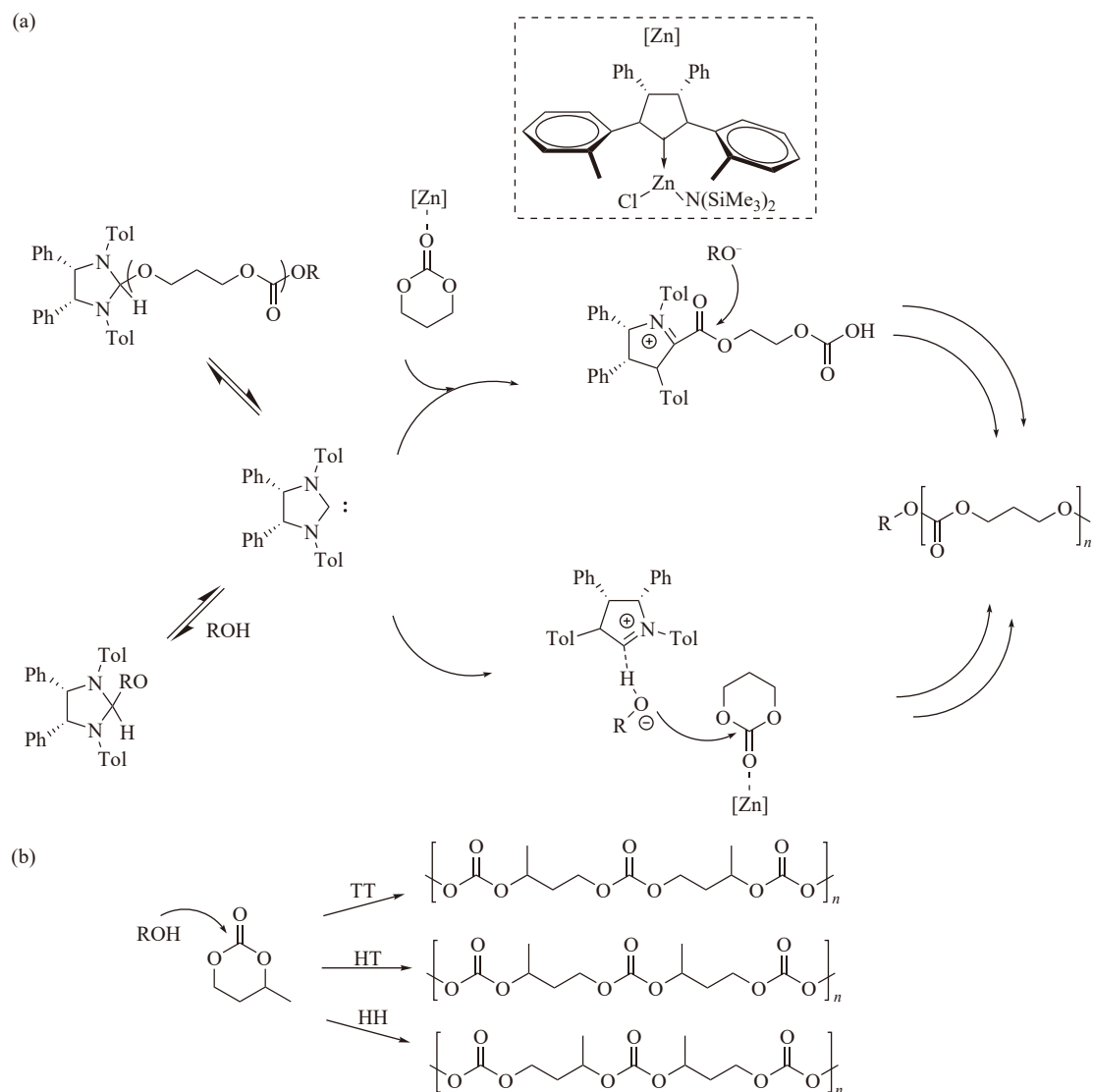


Fig. 6 (a) Hypothesized mechanism for the polymerization of trimethylene carbonate promoted by complex [Zn] and the alcohol used as the cocatalyst (R = Bn); (b) Possible ring-opening sites of 1-methyl trimethylene carbonate and the corresponding polymer microstructures..

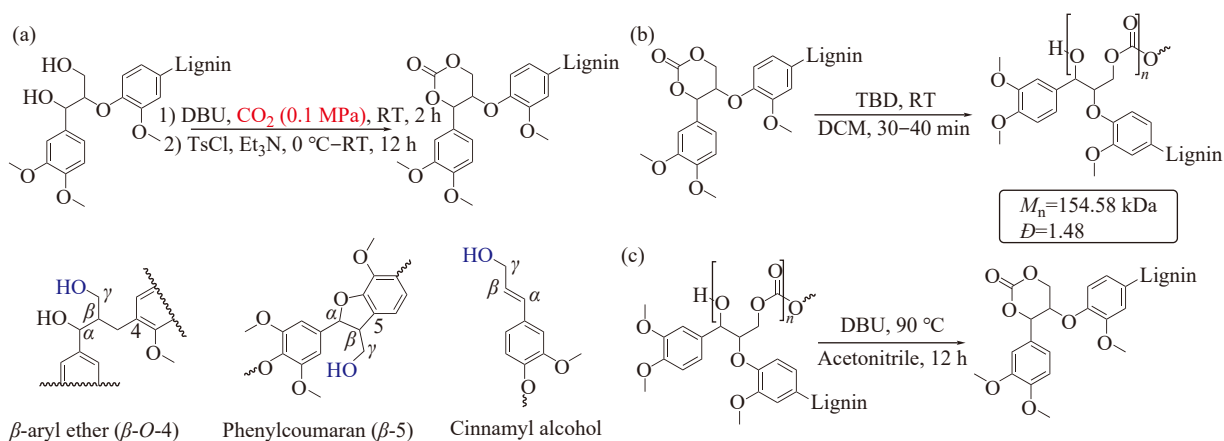


Fig. 7 (a) From synthesizing monomers from CO₂, as well as lignin and the main chemical structural units of lignin with cyclic carbonates; (b) Ring-opening polymerization of lignin-based cyclic carbonate monomers; (c) Chemical depolymerization of lignin-based polymer to cyclic carbonate monomer.

(图 7(b)). 聚合机理遵循酰-氧键断裂模式, 由于木质素单体的结构异质性, 产物呈现区域无规结构. 所得聚碳酸酯展现出优异的热稳定性($T_{d,5\%}=277\text{ }^{\circ}\text{C}$, $T_g=52\text{ }^{\circ}\text{C}$), 源于木质素刚性芳香结构对链段运动的限制. 压缩模量约 418.5 kPa, 10% 应变应力约 47.1 kPa, 模量较同类材料提升 153%, 印证了木质素芳香结构作为刚性“硬段”的增强作用. 在 DBU 催化、 $90\text{ }^{\circ}\text{C}$ 反应 12 h 条件下, 聚碳酸酯解聚回收为原始环状碳酸酯单体, 产率为 76% (图 7(c)). 回收单体在 TBD 催化下再次聚合, 所得再生聚合物与原始聚合物在分子量分布、热稳定性及 T_g 上高度一致, 验证了“聚合物 $\leftrightarrow$ 单体”闭环化学回收的可行性.

1.3 甘油衍生物 1,3-二醇

甘油是生物柴油产业的主要副产物, 来源丰富、价格低廉, 是制备生物基功能单体的重要原料^[88,89]. Martin-Vaca 和 Bourissou 等^[90]以甘油衍生物 1,3-二醇为原料, 合成了含环外亚甲基的六元环碳酸酯单体(exTMC), 通过甲磺酸(MSA)催化实现了 exTMC 与 TMC 的高度无规共聚, 得到结构均匀、功能可调的脂肪族聚碳酸酯. 采用 Buchard 等^[82]报道的“一锅一步法”策略, 成功

合成了 exTMC, 完整保留了环外亚甲基作为后续功能化的反应位点. 单晶结构与 DFT 计算表明, exTMC 的环张力与 TMC 相近(ΔH 分别为 -3.5 和 -2.3 kcal/mol), 聚合驱动力充足. 以 MSA 为有机催化剂, 在 $30\text{ }^{\circ}\text{C}$ 下实现了 exTMC 的可控均聚, 5 h 内转化率高于 96%, 得到分子量可控、分布较窄的聚碳酸酯($M_n=3\text{ kDa}$, $D=1.48$). 机理方面, MSA 催化开环聚合以活性单体(AM)机理为主、活性链端(ACE)机理为辅. AM 路径中质子化单体被亲核进攻实现开环增长, 保证了聚合的可控性(图 8(a)). exTMC 与 TMC 在 MSA 体系下开环共聚, 表现出近乎相等的反应活性($r_{\text{exTMC}}\approx 0.95$, $r_{\text{TMC}}\approx 1.05$), 实现了高无规共聚(图 8(b)). 通过调节投料比与聚合度, 可精确控制共聚物中 exTMC 含量与分子量, 制备链结构均匀的功能化聚碳酸酯. exTMC 的环外亚基为后功能化提供了灵活位点. 聚合后通过硫醇-烯点击化学可直接引入羧基或羟基, 全程无需使用保护基团.

1.4 丙酸酯衍生物 1,3-二醇

Buchard 等^[76,82]开创了 TsCl 与有机碱存在下利用 CO_2 与二醇反应合成环状碳酸酯的方法, 虽然转化率高, 但常伴随着显著的寡聚副反应, 导

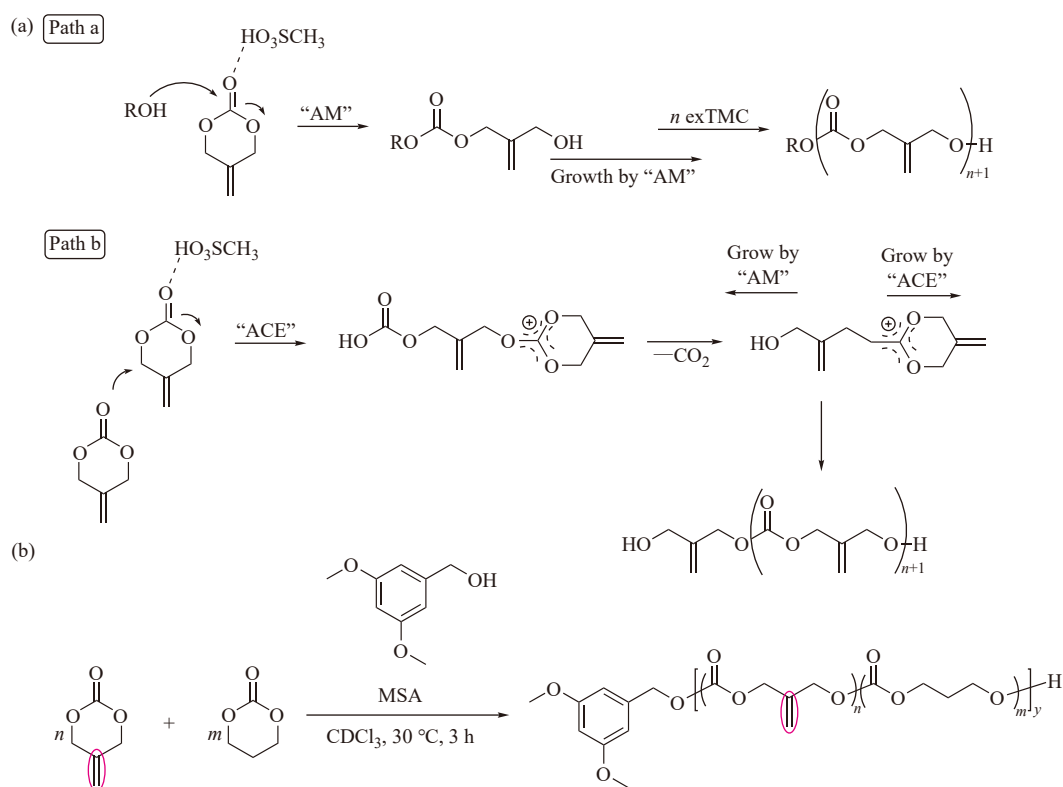


Fig. 8 (a) AM and ACE mechanisms in the MSA catalyzed ring-opening polymerizations of exTMC and structure of the corresponding resulting polymers; (b) Copolymerization reaction of exTMC/TMC.

致单体分离产率偏低. Hedrick 等^[91]通过优化碱催化体系,发现四甲基乙二胺(TMEDA)可作为高效介质,在温和的条件下实现 1,3-二醇转化为六元环状碳酸酯,仅需 10~15 min 实现高转化率(>83%),有效抑制了寡聚副产物的产生,从而大幅度提升单体的合成效率与纯度.该方法适用于以双羟甲基丙酸(bis-MPA)为原料、经酯化或烷基化引入苄基、萘基、氰基等多样化侧链,可串联两步反应,省去中间体分离步骤.所得六元环

碳酸酯在有机催化下表现出良好的可控聚合行为.以 4-甲基苄醇为引发剂、DBU 催化剂、硫脲为助催化剂,室温聚合 1 h 即可实现高转化率(图 9).侧链结构决定聚合物性能,含刚性芳香侧链(苄基、萘基)的聚合物 T_g 达 80~100 °C;含亲水性侧链(氰基、酯基)加速水解降解,而疏水大体积侧链延缓降解.所有聚合物均具有良好生物相容性,在药物递送、抗菌材料等领域具有应用潜力.

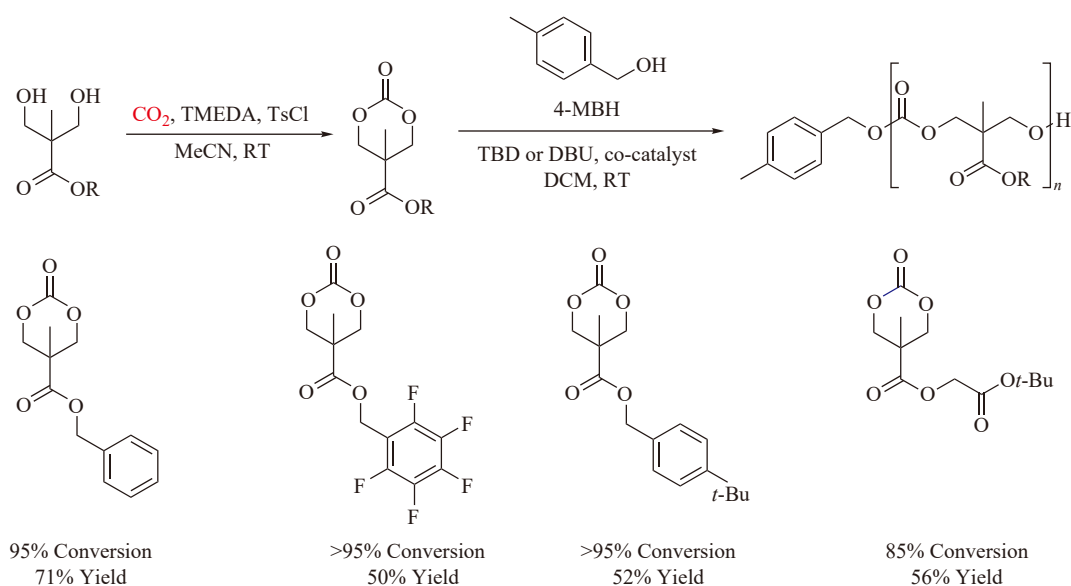


Fig. 9 Synthesis and ring-opening polymerizations of 6MCCs (selected examples) via alcohol activation under alkaline conditions.

1.5 聚羟基脂肪酸酯回收衍生物 1,3-二醇

CO_2 基脂肪族聚碳酸酯发生解聚时,碳酸酯键的水解与脱羧常导致 CO_2 重新释放^[92].近年来兴起的化学回收单体(CRM)策略,为聚合物闭环循环提供了新思路^[93].Wang 和 Zhang 等^[94]利用生物质衍生的二醇和 CO_2 制备化学回收可循环聚碳酸酯的通用温和路线.采用 Hedrick 等^[91]报道的 CO_2 环化策略,以聚羟基脂肪酸酯(PHA)化学回收所得的 5 种不同 α -位烷基取代 1,3-丙二醇为原料,高效合成了系列六元环碳酸酯单体.单晶结构证实, α -位烷基取代基的引入降低了单体的环张力,为后续化学回收提供了热力学基础.以 $t\text{-BuP}_2$ 为催化剂、苄醇为引发剂,在甲苯中 0 °C 下实现了可控开环聚合(图 10(a)).单体转化率 87%~99%,分子量在 5~28 kDa 范围内可调,分散度较低($D < 1.2$).聚合物的区域规整度随取代基位阻增大而提高,异丙基取代单体实现了完美的头-尾连接($X_{\text{reg}} > 0.99$)(图 10(b)).所得聚碳酸酯为无定形材料

($T_g = -25 \sim 3$ °C),热分解温度($T_{d,5\%}$)为 209~245 °C,水接触角为 86.99~97.32°,疏水性随侧链增长而增强.甲基取代聚合物粘接强度达 2.3 N/cm,优于商用丙烯酸粘合剂.随着取代基位阻增大,聚合自由能升高,聚合最高温度(T_c)从 220 °C(甲基)降至 91 °C(异丙基),在 TBD 或 $\text{Sn}(\text{Oct})_2$ 催化下,聚合物可在溶液或本体条件下完全解聚,回收为原始单体,无脱羧副反应发生.解聚速率与单体的平衡温度呈负相关, T_c 最低的异丙基取代聚合物在 1.5 h 内即可完全解聚(图 10(c)).回收单体再次聚合后,所得聚合物与原始聚合物在分子量分布、化学结构及热性能上高度一致,验证了闭环化学回收的可行性,实现了 CO_2 在材料的闭环固定.

2 七元环碳酸酯的合成与开环聚合

六元环和七元环碳酸酯均具有适中的环张力.其中,七元环的环张力高于六元环,为开环聚合提供了更强的热力学驱动力.然而,由于合

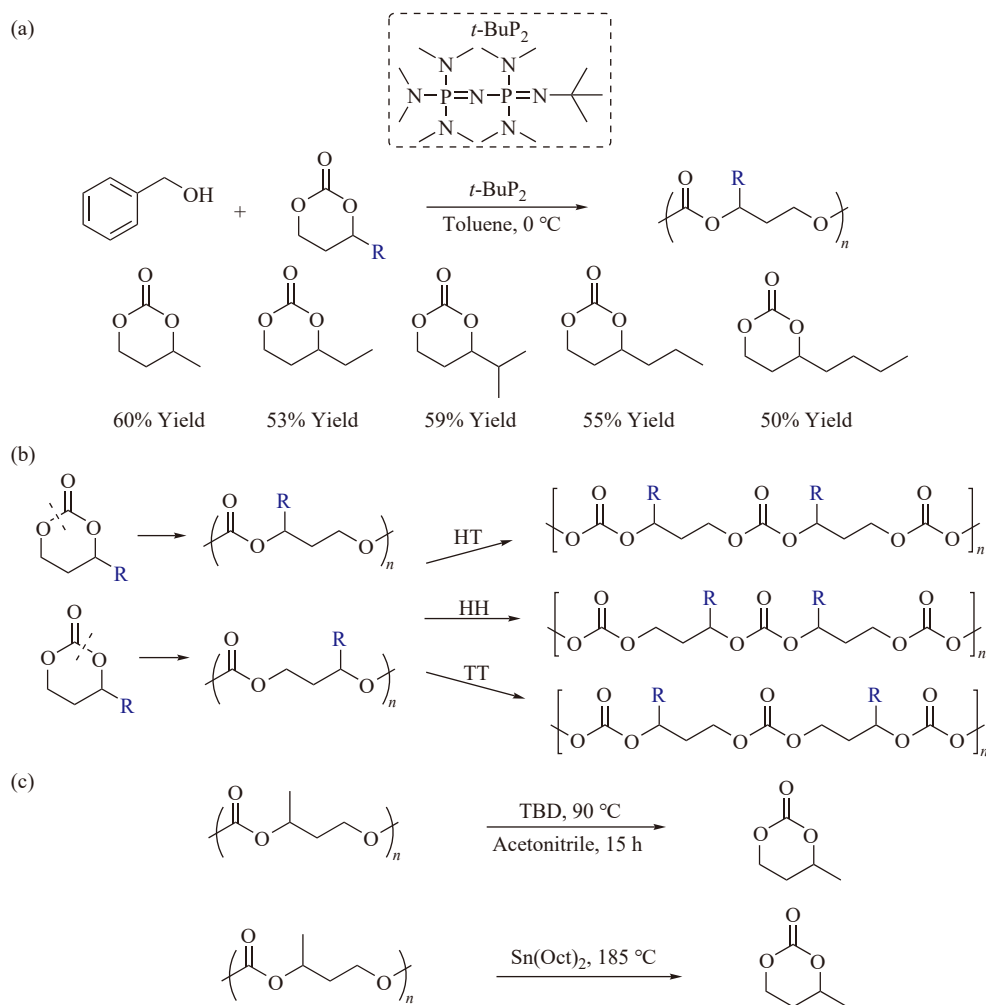


Fig. 10 (a) Ring-opening polymerizations of α -substituted six-membered cyclic carbonates catalyzed by the organic phosphazene base $t\text{-BuP}_2$; (b) Possible ring-opening sites of the synthesized α -substituted six-membered cyclic carbonate monomers and the corresponding microstructures of the resulting polymers (Head-to-Tail (HT), Head-to-Head (HH), Tail-to-Tail (TT)); (c) Solution-phase catalytic depolymerization of isopropyl-substituted polycarbonate enables quantitative monomer recovery, while bulk-phase vacuum depolymerization achieves efficient monomer recovery.

成路线受限、纯化过程复杂，部分七元环碳酸酯在热力学上稳定相差较大，导致相关研究远少于六元环碳酸酯^[95]。本节将介绍以糖类衍生物、环己烷二甲酸/富马酸二甲酯衍生物和呋喃/萘烯衍生物1,4-二醇为原料，总结六元环碳酸酯的合成与开环聚合情况。

2.1 糖类衍生物1,4-二醇

烯烃键的顺反构型对聚合物性能影响显著，例如天然橡胶(顺式)与古塔胶(反式)在弹性上的差异^[96,97]。赤藓糖醇作为一种天然存在的四碳糖醇，是合成1,4-丁烯二醇的理想前体^[98]。Buchard等^[99]合成了一种兼具环状碳酸酯与烯烃的双功能单体，通过开环聚合与开环易位聚合(ROMP)分别实现了烯烃键顺反构型的完全相反调控，获得

力学性能按需可调的新材料。采用Buchard等^[82]报道的“一锅一步法”策略，以51%的产率获得了目标七元环单体，完整保留了二醇的顺式构型(图11(a))。采用2种催化策略实现立体化学的精准调控：以TBD有机催化剂进行开环聚合，保留顺式构型，得到半结晶性聚碳酸酯($T_m=115^\circ\text{C}$)；以Grubbs二代催化剂进行开环易位聚合，获得了95%的反式选择性，得到无定形聚碳酸酯($T_g=-22^\circ\text{C}$)。聚合物中烯烃键可通过Cu(I)/紫外光实现顺反异构化(图11(b))，或通过硫醇-烯点击化学交联制备热固性树脂。进一步结合2种聚合方式，以顺式-1,4-丁烯二醇为链转移剂，一锅法合成了顺-反-顺三嵌段共聚物。顺式聚合物为半结晶硬质材料，反式聚合物为粘弹性软质材料，三嵌段

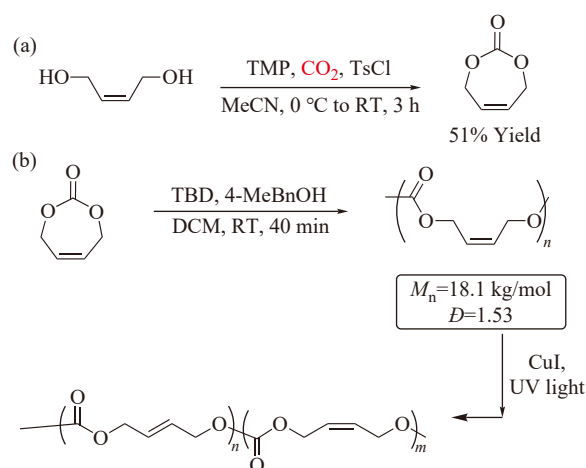


Fig. 11 (a) Synthesis of seven-membered cyclic carbonates containing olefins; (b) Ring-opening polymerization and post-functionalization of seven-membered cyclic carbonates containing alkenes.

共聚物兼具硬软链段，具有热塑性弹性体应用前景。

2.2 环己烷二甲酸/富马酸二甲酯衍生物 1,4-二醇

通过调节单体的环张力、取代基结构或引入稠环结构，可有效调控聚合物热性能与化学回收性能^[100~102]. Cai 和 Zhu 等^[103]设计合成了一类反式稠合七元环碳酸酯单体，通过钪配合物(Y1)催化实现超高活性开环聚合，制备出兼具高热稳定性与可化学回收性能的聚碳酸酯。以反式-1,2-环己烷二甲酸或反式-4-环己烯-1,2-二甲酸二甲酯为起始原料，经氢化铝锂(LiAlH₄)还原获得相应二醇，采用 Buchard 等^[82]报道的“一锅一步法”策略，以 72%~76% 的产率获得目标单体(图 12(a)). 该路线完整保留了反式构型的手性特征，所引入的环内双键为后续功能化提供了反应位点。反式

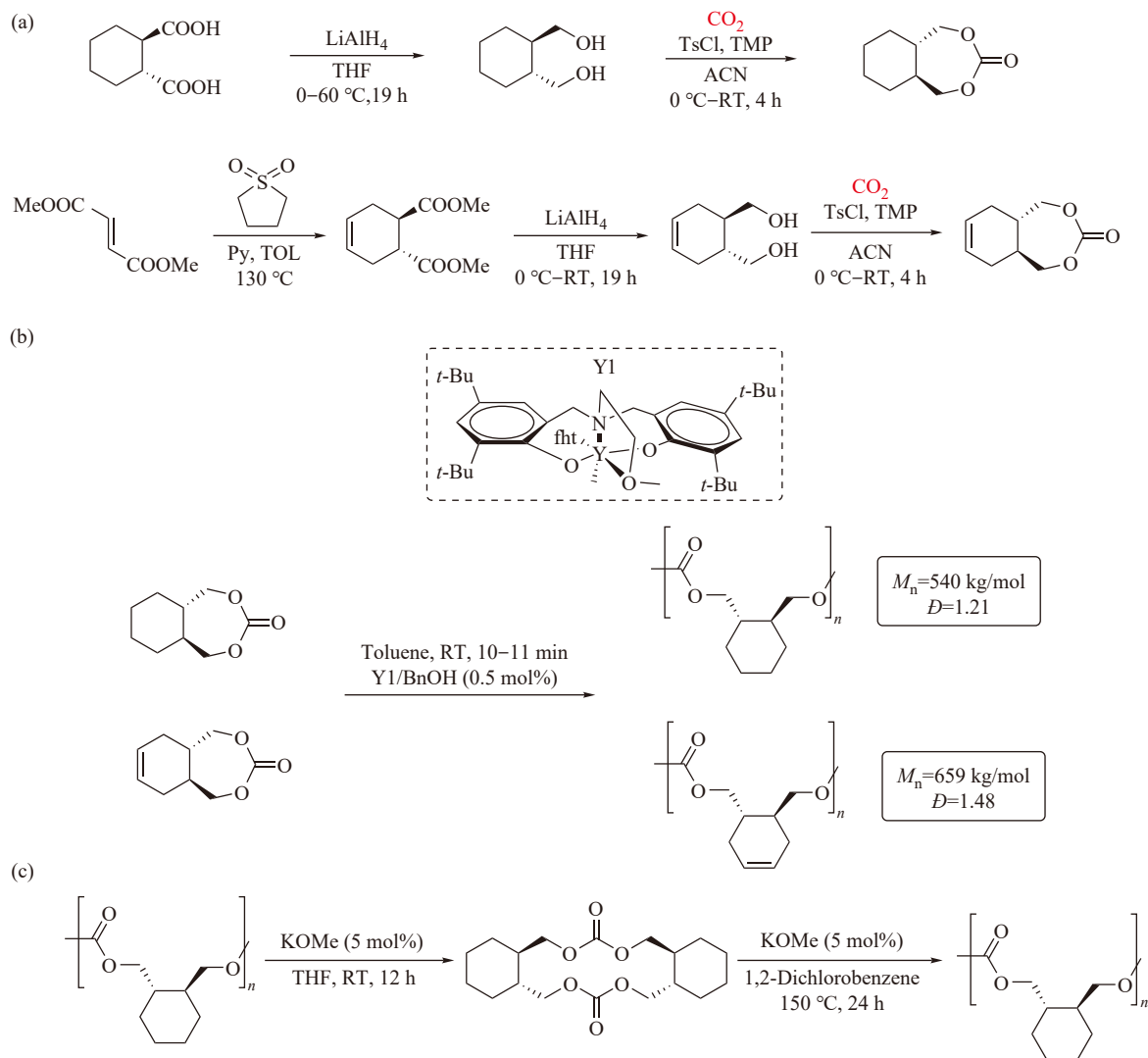


Fig. 12 (a) Synthesis of trans-fused seven-membered cyclic carbonate monomers; (b) Ring-opening polymerizations using [Y1]/BnOH as catalyst; (c) Chemical recycling process of polycarbonate depolymerizing into dimers under MeOK catalysis.

稠合结构赋予七元环适度的环张力, 构成开环聚合的热力学驱动力, 同时也为后续解聚为二聚体而非单体的特殊行为提供了结构基础. 以 Y1 为催化剂, 在室温下通过配位-插入机理实现超高活性聚合. 30 s 内转化率可达 100%, 转化频率(TOF) 高达 $6 \times 10^5 \text{ h}^{-1}$, 催化剂用量可低至 50 ppm. 聚合物分子量随单体与引发剂投料比的增加而线性增长, 最高可达 673 kDa, 分子量分布保持窄分散特征 ($D=1.17\sim1.48$) (图 12(b)). 含双键的聚合物可通过光交联或硫醇-烯点击化学实现高效后功能化, 接枝效率最高达 95%. 所得聚碳酸酯均表现出优异的热稳定性, $T_{d,5\%}$ 热分解温度高于 300°C , 最高可达 325°C . T_g 为 $32\sim39^\circ\text{C}$, 交联后可提升至 54°C . 在甲醇钾(MeOK)催化下, 聚合物可完全解聚为二聚体, 产率约 80%. 解聚过程表现出立体选择性, 外消旋聚合物解聚生成热力学更稳定的内消旋二聚体, 而手性聚合物则解聚为相应的手性二聚体. 二聚体在 150°C 下经碱催化可再次聚合, 回收聚合物与原始聚合物在分子量分布、化学结构及热性能上高度一致(图 12(c)). 该策略避免了直接解聚为单体过程中常见的脱羧副反应.

Cai 和 Zhu 等^[104]进一步合成了顺式或反式稠合七元环碳酸酯, 建立了有机催化开环聚合体系, 制备出分子量可控、热稳定性良好的聚碳酸酯. 以顺/反式环己烷/环己烯二甲酸酐为原料, 经 LiAlH_4 还原获得相应二醇, 基于 Buchard 等^[82]报道的“一锅一步法”策略, 合成了顺式或反式稠合七元环碳酸酯(C6DO、C6HDO、T6DO、T6HD). 系统评估了有机碱 TBD、DBU 和有机酸二苯基磷酸(DPP)的催化性能(图 13), TBD 在室温下对 T6DO 的聚合表现出最优活性, 所得聚合物分子量可控、分散度低($D=1.06$). 动力学研究表明聚合遵循一级动力学, 分子量与转化率呈线性关系, 证实了活性聚合特征. 在 90°C 下聚合时, TBD 的催化活性进一步提升, TOF 最高达 10^3 h^{-1} , 聚合物分子量最高可达 151 kDa. 通过顺序加料法成功制备了嵌段共聚物, 分子量分别为 41.7 kDa 和 38.0 kDa, 分散度均低于 1.14. 所得聚碳酸酯均为无定形材料, T_g 在 $24\sim35^\circ\text{C}$ 范围内, $T_{d,5\%}$ 热分解温度在 $281\sim312^\circ\text{C}$ 之间.

2.3 呋喃/萘烯衍生物 1,4-二醇

获得具有可调性质的高性能聚碳酸酯和多环烯烃, 需要设计兼具环张力和反应活性的双功能

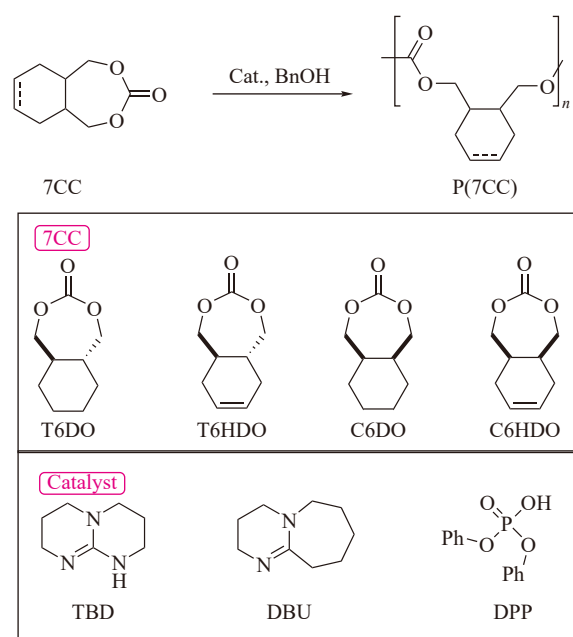


Fig. 13 Organocatalytic ring-opening polymerizations of 7CCs.

单体^[105,106]. Cai 和 Zhu 等^[107]成功合成了一系列基于生物质原料的双功能七元环碳酸酯单体, 兼具开环聚合与开环易位聚合的能力, 实现了聚碳酸酯与聚环烯烃的可控制备及性能调控. 以生物质来源的马来酸酐与呋喃或 α -萘品烯为原料, 通过 Diels-Alder 环加成构建刚性双环骨架, 经 LiAlH_4 还原和 CO_2 环化, 高效合成了一系列七元环碳酸酯双功能单体(图 14(a)). 保留的双键为后续开环易位聚合和点击化学功能化提供了反应位点. 对比了有机催化剂与金属配合物的催化行为(图 14(b)). 采用锌基配合物(Zn-1)催化, 实现了室温下的快速可控开环聚合, 部分单体在 0.01% 超低催化剂用量下仍可达 $2.8 \times 10^4 \text{ h}^{-1}$ 的高转化频率. 聚合物分子量最高可达 991 kDa. 含碳碳双键的单体在 Grubbs 催化剂作用下可快速进行 ROMP, 得到分子量可控、分散度低的聚环烯烃. 所得聚碳酸酯的 T_g 分别为 85 和 99°C , 显著高于传统七元环碳酸酯聚合物; 聚环烯烃的 T_g 高达 194°C . 通过硫醇-烯点击反应引入柔性烷基侧链后, 聚合物的 T_g 可降至 29°C , 断裂伸长率达 305%, 拉伸强度为 11.9 MPa , 展现出与低密度聚乙烯相当的力学行为^[108]. 所得聚碳酸酯在碱性条件下可完全水解为相应的二醇单体, 回收率 85%~95% (图 14(c)). 回收的二醇经再环化可重新获得单体, 再次聚合得到分子量与热性能一致的再生聚合物, 实现了从生物质单体到聚合物再回单体的闭环循环.

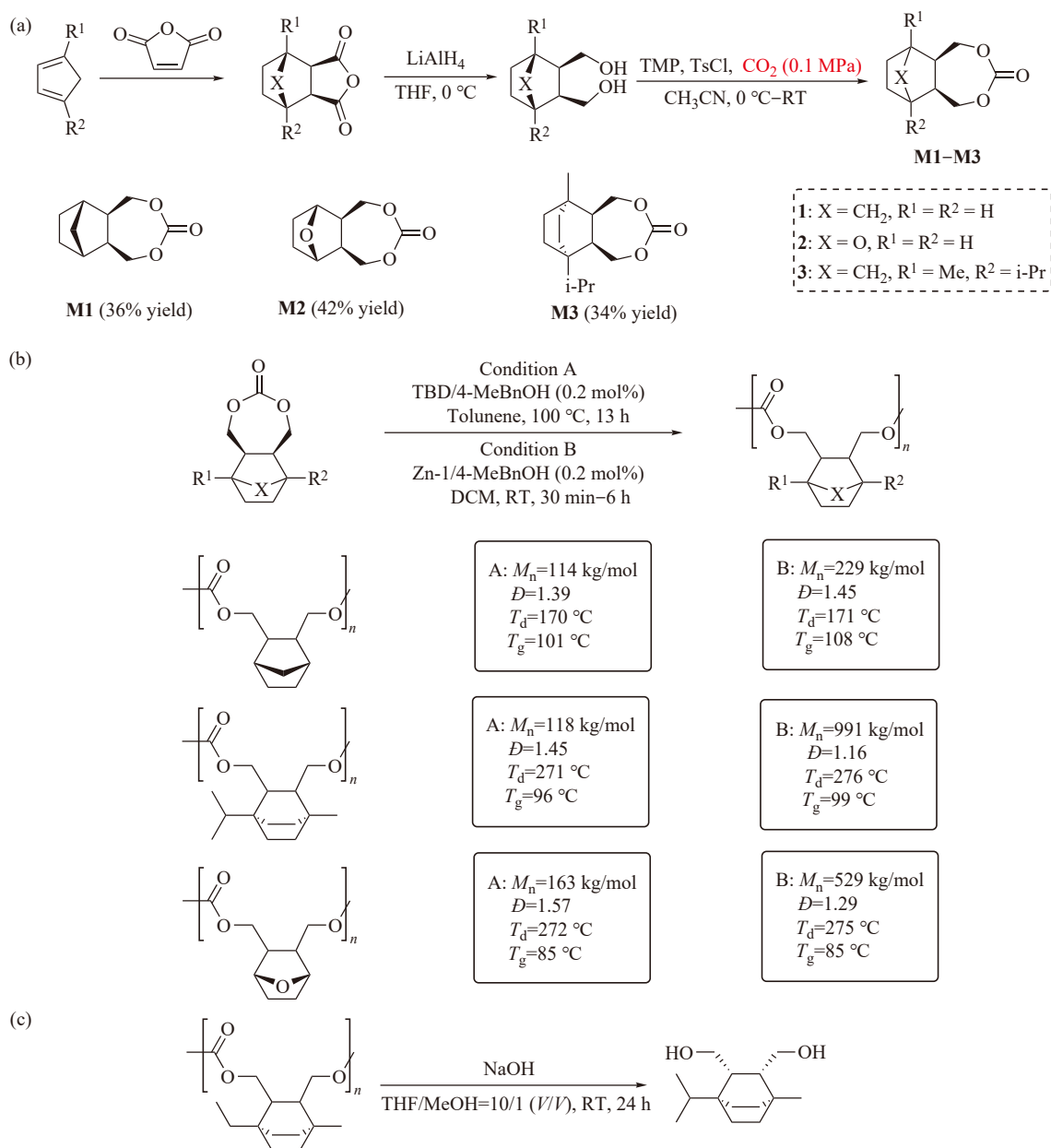


Fig. 14 (a) Synthesis of bifunctional seven-membered cyclic carbonate monomers; (b) Comparison between organic and metal-mediated ring-opening polymerizations of seven-membered cyclic carbonates; (c) Simple hydrolysis of polymer by aqueous NaOH.

3 八元环碳酸酯的合成与开环聚合

迄今为止, 脂肪族聚碳酸酯的合成主要集中于五元环至七元环碳酸酯开环聚合, 八元环碳酸酯相对最少^[109-111]. 八元环碳酸酯的合成与开环聚合长期面临环化效率低、副产物难分离等瓶颈. 本节将介绍基于1,5-二醇构建的八元环碳酸酯单体, 总结克服这些挑战的创新合成策略(如混合碱体系)以及实现可控聚合的催化方法.

Buchard 等^[76,82]的方法用于含氮1,5-二醇底

物时, 常伴随显著的寡聚副反应及产物分离困难等问题, 导致八元环状碳酸酯单体的合成效率受限. Hedrick 等^[91]发展了一种基于TMEDA与三乙胺(TEA)混合碱体系的高效合成策略. 以二乙醇胺(DEA)为起始原料, 经*N*-烷基化反应引入苄基、萘基、酯基等侧链, 在TMEDA与TEA混合碱存在下, 以TsCl为活化剂、CO₂为碳源, 在0 °C至室温下反应1~1.5 h, 以45%~85%的产率得到一系列功能化八元环状碳酸酯单体(图15(a)). 与六元环合成中单独使用TMEDA不同, 混合碱体系可

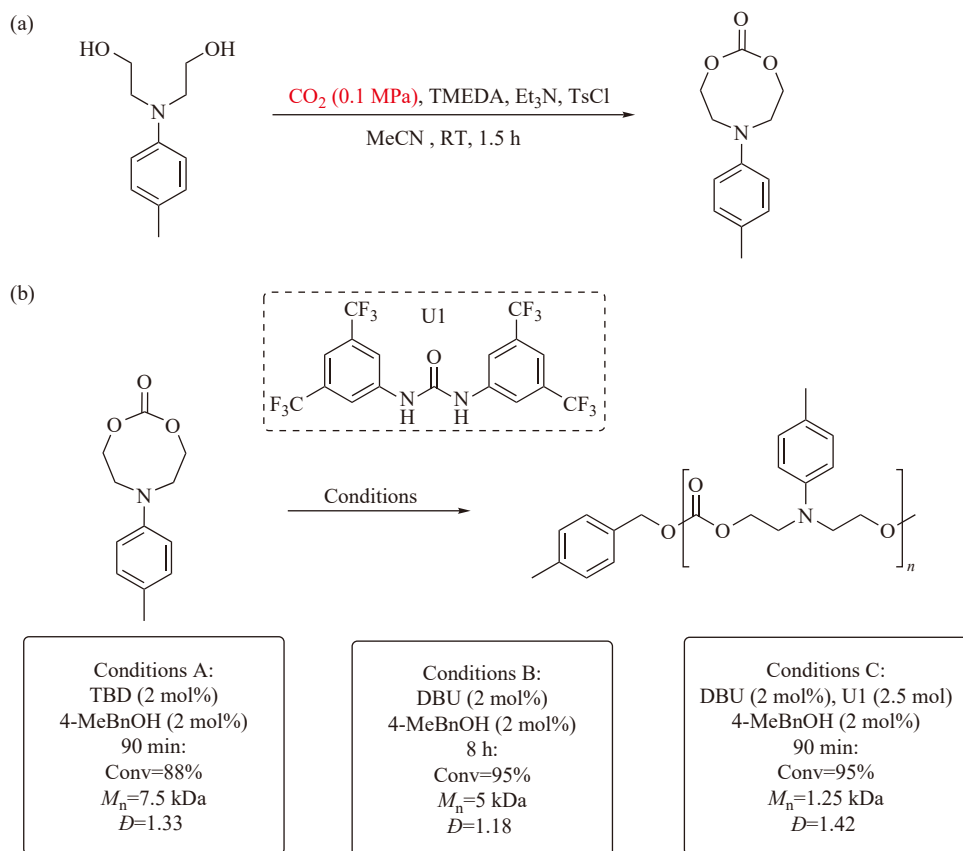


Fig. 15 (a) Route for synthesizing nitrogen-containing eight-membered cyclic carbonates using a TMEDA/ Et_3N mixed base strategy; (b) Effects of different organocatalytic systems (TBD, DBU, and DBU/U1 cooperative catalysis) on the anionic ring-opening polymerizations of eight-membered cyclic carbonates.

有效稀释铵盐副产物生成, 反相加料顺序进一步抑制寡聚副反应. 针对单体中叔氮原子对催化循环的干扰, 采用 DBU/脲共催化剂(U1)体系, 在四氢呋喃(THF)中实现活性可控聚合(图 15(b)). 所得聚合物的 M_n 可达 16.3 kDa, 分散度低($D=1.18$). 该体系可控聚合的关键在于 THF 可抑制链端亲核活化与阴离子活化机制的竞争, 避免高分子量肩峰生成. 八元环聚碳酸酯的 T_g 可通过 N -取代基调控: 芳香族取代基(萘基、联苯基)赋予较高 T_g , 烷基取代基则降低 T_g . 主链碳酸酯键可水解降解, 侧链亲水性调节降解速率. 上述聚合物具有良好的生物相容性, 在药物递送、抗菌材料等领域展现出应用潜力.

4 结论与展望

基于二氧化碳与二醇反应环碳酸酯的合成与开环聚合已成为高分子化学和绿色化学等领域的重要方向, 取得了阶段性成果. 通过二醇的结构设计, 获得相应的功能化环碳酸酯单体, 进一步

通过催化可控开环聚合, 制备一系列结构多样、性能可调的脂肪族聚碳酸酯材料, 不仅实现了温室气体的资源化利用, 也为诸多领域提供了性能优异的可持续高分子材料. 展望未来, 基于二氧化碳/二醇反应环碳酸酯的合成与开环聚合研究挑战与机遇并存, 建议关注以下方向: (1) 单体设计, 尽管已开发出六元、七元及八元环碳酸酯, 但是部分单体的合成步骤仍较繁琐、产率偏低, 特别是大环单体的高效制备仍需突破, 亟待合成新的环碳酸酯单体结构, 发展高效单体制备方法; (2) 催化体系, 现有金属催化和有机催化体系对大环及部分功能化环碳酸酯单体的聚合控制能力仍有不足, 亟待深入理解催化开环聚合机理、发展高活性、高选择性的催化体系, 实现对开环聚合过程的精准调控; (3) 性能与应用, 已报道聚碳酸酯的综合性能尚无法完全满足实际应用的要求, 主要研究仍处于实验室探索阶段, 亟待加强产学研合作, 系统阐明材料的构效关系, 以应用为导向, 开发高附加值聚碳酸酯新材料.



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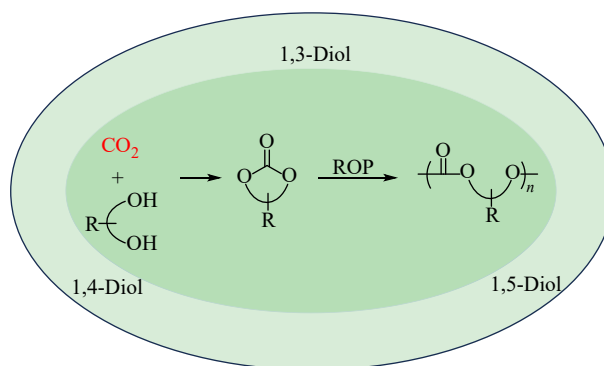
Review

Synthesis and Ring-opening Polymerizations of Cyclic Carbonates Derived from Carbon Dioxide/Diol Reactions

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Abstract The high-value utilization of carbon dioxide (CO₂) for the conversion into fine chemicals and polymer materials have been paid much attention in polymer science and green chemistry. Among them, the reaction of CO₂ with diols to produce cyclic carbonates represents an important direction. Through the catalytic controlled ring-opening polymerizations of cyclic carbonates, polycarbonates with different structures and properties can be prepared. This review focuses on synthesis and ring-opening polymerizations of cyclic carbonates derived from CO₂/diol reactions. The reactions of CO₂ with 1,3-diol derivatives, 1,4-diol derivatives, and 1,5-diol derivatives were summarized in order with the target products of six-membered, seven-membered, and eight-membered cyclic carbonates. Catalytic ring-opening polymerizations of these obtained cyclic carbonates into polycarbonates were highlighted. Moreover, the challenges and opportunities in the related fields were discussed.



Keywords Carbon dioxide; Diol; Cyclic carbonate; Ring-opening polymerization; Polycarbonate

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