浙江大学高校教师专业技术高级职务申报表

姓名	张兴宏
单位	高分子科学与工程学系
所在学科	高分子化学与物理
现专业技术职务	副教授
申请专业技术职务	教授
申请研究生招生资格	不申请(已具有相应资格)
联系电话	13588846711
Email	xhzhang@zju.edu.cn

填报日期：2015年 9月

一、基本情况

姓名	张兴宏	性别	男
出生年月	19771025	国籍	中国
兼任党政职务	高分子科学所副所长	现专业技术职务	副教授
任职时间	20091228	所在二级学科	高分子化学与物理
申请研招资格	不申请(已有相应资格)	申请专业技术职务	教授
现工作单位	高分子科学与工程学系		
从事专业及专长	催化与可控聚合		
联系电话	13588846711	Email	xhzhang@zju.edu.cn
最后学历、毕业学校、所学专业、学位及取得时间、导师姓名	博士研究生，浙江大学，高分子化学与物理，博士，2006年6月，导师：戚国荣教授。		
主要学术兼职	浙江省粘接技术协会常务理事（2014-2019）； 《粘接》杂志特约撰稿人（2015-2017）。		

个人简历（要求从大学开始，采用时间倒序方式填写，时间不间断）

“学历进修经历”填写格式：自何年月至何年月，在何地，何学校（单位），何专业，学习、进修，导师;

学习进修经历	2003/3 - 2006/6，浙江大学，高分子化学与物理，理学博士，导师：戚国荣教授 2000/9 - 2003/3，汕头大学，工业催化，工学硕士，导师：刘晓暄教授和吴光国教授 1996/9 - 2000/7，阜阳师范学院，化学，学士。

“工作经历”填写格式：自何年月至何年月，在何地、何学校（系所）、何单位任职，任何职（海外职位英文表述）；

工作经历	2009/12 - 至今，浙江大学，高分子科学与工程学系，副教授 2006/7 - 2009/12，浙江大学，高分子科学与工程学系，讲师 2012/7 - 2013/8，美国伊利诺伊香槟分校，贝克曼研究所，访问学者（国家留学基金委资助），合作教授Jeffrey S. Moore。

二、申请人标志性工作(不超过300字)

长期专注于高分子化学的教学与科研.获2014年浙大教学比赛二等奖. 系统研究了催化一碳单体可控共聚合: 提出了锌羟基催化C1聚合理论,实现非均相高效高选择性催化C1/环氧化物共聚,建立了一釜一步高效合成结晶性多嵌段和刷状CO_2基共聚物的新方法.以第一和第一通讯作者在Chem. Sci.(1),Macromolecules(7)和Polymer(5)等期刊发表25篇论文(IF>3的22篇);影响因子总和94,平均3.8.至今他引共360次.获得了最高效的CO_2共聚催化剂并完成中试生产.授权中国发明专利12项和美国发明专利1项;年均受邀为Macromolecules等期刊审稿30篇以上;受TOP期刊Polymer邀请撰写Feature Article,受国际知名学者邀请撰写专著;受邀参加国内外会议口头报告9次. 获2016年浙江省杰出青年基金资助.相关研究已在国内外产生明显影响.

三、申请人任现职以来近五年主要业绩

3.1 教学与人才培养情况

1、共开设课程6门，课程教学时数共计208学时。其中本科生课程4门，课程教学时数128学时。开课情况如下：

(填写格式：教学年度，课程名称，授课对象，学生数，学时数，考核结果)

本科生课程：
2010-2011-1 企业实习 本科生 91 +2
2011-2012-1 高分子化学实验 本科生 105 0.0-4.0
2013-2014-1 高分子化学实验 本科生 91 0.0-4.0
2013-2014-1 实验室安全 本科生 89 +1
2014-2015-1 高分子化学实验 本科生 94 0.0-4.0
2014-2015-1 实验室安全 本科生 93 +1
2015-2016-1 实验室安全 本科生 96 +1
2014夏短 本科生高级实验课程 本科生 2
2015夏短 本科生高级实验课程 本科生 1
研究生课程：
2010-2011秋 高等物理化学 研究生 16学时
2011-2012秋 高等物理化学 研究生 16学时
2013-2014秋 高等物理化学 研究生 16学时
2014-2015秋 高等物理化学 研究生 16学时
2013-2014秋 实验室安全 研究生 16学时
2014-2015秋 实验室安全 研究生 16学时

2、指导本科生毕业论文(设计)12人(请列出姓名、专业、年级)

(填写格式：姓名，专业，年级)

罗铭 高分子材料与工程 2007
孟渊 高分子材料与工程 2007
周鑫 高分子材料与工程 2007
陈郁栋 高分子材料与工程 2007
王浩 高分子材料与工程 2007
崔剑峰 高分子材料与工程 2008
韩旭 高分子材料与工程 2008
霍菲 高分子材料与工程 2008
李洋 高分子材料与工程 2009
国庆 高分子材料与工程 2010
罗杰 高分子材料与工程 2011
王宇翔 高分子材料与工程 2011

3、指导研究生5名，协助指导博士生4人(请列出研究生姓名、专业、年级)

(填写格式：研究生姓名，专业，年级)

张江凤 高分子化学与物理 2010硕士生
洪佳丽 高分子化学与物理 2011硕士生
张滢滢 高分子化学与物理 2012硕士生
王利军 高分子化学与物理 2013硕士生
刘斌 高分子化学与物理 2014硕士生
李洋 高分子化学与物理 2013直博生（协助指导）
罗铭 高分子化学与物理 2011直博生（协助指导）
魏人建 高分子化学与物理 2011转博（协助指导）

孙学科 高分子化学与物理 2007直博生（协助指导）

3.2 代表性论文、著作情况

共发表论文33篇。其中作为第一作者或通讯作者25篇，请按照您认为最具代表性、重要性或影响力的顺序列出：(不超过15篇)

(填写格式：所有作者姓名（通讯作者名字上用“*”标示），论文题目，发表期刊名称，出版年月，卷，期，起止页码，检索情况，期刊影响因子，他引次数)

1. Yang Li, Jiali Hong, Renjian Wei, Yingying Zhang, Zaizai Tong, Xinghong Zhang*, Binyang Du, Junting Xu, Zhiqiang Fan, Highly efficient one-pot/one-step synthesis of multiblock copolymers from three-component polymerization of carbon dioxide, epoxide and lactone. **Chemical Science**, 2015, 6(2), 1530-1536, SCI, IF = 9.211,他引1次。

2. Xinghong Zhang*, Renjian Wei, Yingying Zhang, Binyang Du, Zhiqiang Fan, Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc–Cobalt(III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures. **Macromolecules**, 2015, 48(3), 536-544, SCI, IF = 5.800，他引0次。

3.Yuqin Min, Shuyun Huang, Yuxiang Wang, Zhijun Zhang, Binyang Du, Xinghong Zhang*, Zhiqiang Fan. Sonochemical Transformation of Epoxy–Amine Thermoset into Soluble and Reusable Polymers. **Macromolecules**, 2015, 48(2), 316-322, SCI, IF = 5.800，他引0次。

4. Ming Luo, Xinghong Zhang*, Darensbourg, D. J.*, An Investigation of the Pathways for Oxygen/Sulfur Scramblings during the Copolymerization of Carbon Disulfide and Oxetane. **Macromolecules**, 2015, 48(16), 5526-5532, SCI, IF = 5.800，他引0次。（浙大第一单位）

5. Ming Luo, Xinghong Zhang*, Darensbourg, D. J.*, An Examination of the Steric and Electronic Effects in the Copolymerization of Carbonyl Sulfide and Styrene Oxide. **Macromolecules**, 2015, 48(16), 6057-6062, SCI, IF = 5.800，他引0次。（浙大第一单位）

6. Renjian Wei, Xinghong Zhang*, Binyang Du, XueKe Sun, Zhiqiang Fan, Guorong Qi, Highly Regioselective and Alternating Copolymerization of Racemic Styrene Oxide and Carbon Dioxide via Heterogeneous Double Metal Cyanide Complex Catalyst, **Macromolecules**, 2013, 46(9), 3693-3697, SCI, IF = 5.800,他引7次。

7. Ming Luo, Xinghong Zhang*, Bingyang Du, Qi Wang, Zhiqiang Fan, Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Racemic Propylene Oxide. **Macromolecules**, 2013, 46(15), 5899-5904, SCI, IF = 5.800,他引2次。

8. JiangFeng Zhang, Weimin Ren, Xueke Sun, Yuan Meng, Binyang Du, Xinghong Zhang,* Fully Degradable and Well-Defined Brush Copolymers from Combination of Living CO2/Epoxide Copolymerization, Thiol–Ene Click Reaction and ROP of ε-caprolactone. **Macromolecules**, 2011, 44(24), 9882-9886, SCI, IF = 5.800,他引15次。

9. Ming Luo, Xinghong Zhang,* Binyang Du, Qi Wang, Zhiqiang Fan, Well-defined high refractive index poly(monothiocarbonate) with tunable Abbe's numbers and glass-transition temperatures via terpolymerization. **Polymer Chemistry**, 2015, 6(27), 4978-4983, SCI, IF = 5.520,他引0次。

10. Yingying Zhang, Yang Li, Xianjing Zhou, Xinghong Zhang*, Binyang Du, Zhiqiang Fan, Synthesis of an Amphiphilic Brush Copolymer by a Highly Efficient “Grafting onto” Approach via CO_2 Chemistry. **Macromolecular Rapid Communications**, 2015, 36(9), 852-857, SCI, IF = 4.941,他引0次。

11. Xinghong Zhang*, Renjian Wei, Xueke Sun, Jiangfeng Zhang, Binyang Du, Zhiqiang Fan, Guorong Qi, Selective copolymerization of carbon dioxide with propylene oxide catalyzed by a nanolamellar double metal cyanide complex catalyst at low polymerization temperatures, **Polymer**, 2011, 52(24), 5494-5502, SCI, IF = 3.562，他引10次。

12. Xueke Sun, Xinghong Zhang*, Shang Chen, Binyang Du, Qi Wang, Zhiqiang Fan, Guorong Qi, One-pot terpolymerization of CO2, cyclohexene oxide and maleic anhydride using a highly active heterogeneous double metal cyanide complex catalyst, **Polymer**, 2010, 51(24), 5719-5725, SCI, IF = 3.562, 他引18次。

13. Xueke Sun, Xinghong Zhang*, Renjian Wei,Binyang Du, Qi Wang, Zhiqiang Fan, Guorong Qi. Mechanistic insight into initiation and chain transfer reaction of CO2/cyclohexene oxide copolymerization catalyzed by zinc-cobalt double metal cyanide complex catalysts. **Journal of Polymer Science Part A: Polymer Chemistry**, 2012, 50, 2924-2934, SCI, IF = 3.113,他引9次。

14. Yuan Meng, Xinghong Zhang*, Binyang Du, Boxuan Zhou, Xin Zhou, Guorong Qi. Thermosets with core–shell nanodomain by incorporation of core crosslinked star polymer into epoxy resin. **Polymer**, 2011, 52, 391-399, SCI, IF = 3.562, 他引18次。

15. Renjian Wei, Xinghong Zhang*, Binyang Du, Zhiqiang Fan, Guorong Qi. Synthesis of bis (cyclic carbonate) and propylene carbonate via a one-pot coupling reaction of CO_2, bisepoxide and propylene oxide. **RSC Advances**, 2013, 3, 17307-17313, SCI, IF = 3.84，他引6次。

出版著作教材共2本，总字数为5万字，其中为主编、副主编出版全国统编教材0本，省部重点、规划教材共0本：（不超过10本）

(填写格式：所有作者姓名，书名，著作类型，出版地，出版社名称，出版年月，个人字数/总字数)

1, Yuan Meng, Xinghong Zhang*. Nanostructure Formation in Thermoset/Block Copolymer and Thermoset/Hyperbranched Polymer Blends (pages 161-194, Chapter 6 of book: Nanostructured Polymer Blends, edited by Sabu Thomas, Robert Shanks et al), Elsevier Inc, 2013-12, ISBN(ASIN): 1455731595, 条形码: 978-1-4557-3159-6, William Andrew publishing(出版社); 丛书名: Micro & Nano Technologies

2, Yuan Meng, Xinghong Zhang*. Nanostructured epoxy composites (Chapter 3 of book: Micro and Nanostructured Epoxy/Rubber Blends), Wiley-VCH Verlag GmbH, 2014-02. ISBN(ASIN) 3527333347,条形码：978-3-527-33334-9, Germany.

3.3 承担或参与的主要科研、教改项目

1、共参加项目19项，其中纵向项目7项，横向项目12项；
主持项目到校总经费**499.29**万元，其中纵向项目到校经费**176.6**万元，横向项目到校经费**322.69**万元。

2、作为项目负责人承担项目16项，其中纵向项目6项，横向项目10项。具体项目如下(请按您认为最具代表性、重要性或影响力的顺序列出)：(不超过15项)

(填写格式：项目名称，项目性质及来源，项目编号，项目经费（括号内为本人实际承担经费，单位万元），起始年月，终止年月，项目成员）)

以下项目均为负责人。

1、一釜合成多嵌段CO_2基共聚物及其结构与性能、国家自然科学基金面上项目、21474083、88（已到款39.6）、2015/01-2018/12、在研、主持。

2、氧硫化碳-环氧化物可控催化共聚及机理研究、国家自然科学基金面上项目、21274123、86（已到款86）、2013/01-2016/12、在研、主持。

3、基于CO_2/环氧化物可控共聚技术合成可降解的聚合物分子刷、国家自然科学基金面上项目、21074106、36（已到款36）、2011/01-2013/12、已结题、主持。

4、低碳路线合成可降解型聚碳酸酯多元醇和聚氨酯，纵向，浙江省科技厅，G20100284，15（已到款15），2011-01-01，2012-12-31，已结题、主持。

5、CO_2固定为碳酸二甲酯的绿色催化合成新方法，纵向，浙江省自然科学基金办公室，J20091484，8（已到款8），2010-01-01，2012-12-31，已结题、主持.

6、阻燃聚酯薄膜专用聚酯树脂的合成技术，横向，江苏裕兴薄膜科技股份有限公司，H20121522，100（已到款55），2012-06-11，2013-12-31，张兴宏（主持）、徐君庭、杜滨阳、戚国荣。

7、印制电路板用特种油墨，横向，建滔化工集团建滔积层板（昆山）有限公司，I20120066，100（已到款30），2012-06-01，2014-06-30，张兴宏（主持）、杜滨阳.

8、环保型无卤阻燃光固化无溶剂漆研究，横向，苏州市明大高分子科技材料有限公司，H20121811，20（已到款8），2012-06-19，2014-05-31，张兴宏（主持）、杜滨阳。

9、环保型高性能VPI浸渍树脂研究，横向，吴江市太湖绝缘材料有限公司，H20120351，10（已到款5），2012-02-15，2013-02-28，张兴宏（主持）.

10、含芳香席夫碱和醚键结构的二元酚衍生物及其制备方法和应用（200610155092.6），横向，依利安达电子（昆山）有限公司，H20110691，10（已到款10），2011-03-20，2016-03-19，张兴宏（主持），专利实施项目。

11、高耐热/高导热环保型电子基板的低成本制造技术，横向，香港建滔化工集团，I20140043，110（已到款20），2014-06-01，2016-05-31，张兴宏（主持）.

12、覆铜板制造及高性能化研究，横向，香港建滔化工集团建滔积层板（昆山）有限公司，I20100131，120（已到款105），2010-11-30，2014-10-30，张兴宏（主持）、杜滨阳、戚国荣。

13、聚碳酸酯多元醇合成关键技术中试，横向，南阳中聚天冠低碳科技有限公司，H20151033，100（已到款50），2015-05-18，2017-05-31，张兴宏（主持）.

14、聚碳酸酯多元醇精制技术，横向，南阳中聚天冠低碳科技有限公司，H20151032，30（10），2015-05-18，2016-12-31，张兴宏（已到款主持）.

15、高分子化学实验课程的交互式教学研究，浙江省2013年高等教育课堂教学改革项目(kg2013017)，省教改项目，主持人，2014-2015；学校1万元，系配套4万元，1/5。

3.4 获得的重要成果奖励

共获成果奖14项，其中教材奖0项，教学成果奖0项，科研成果奖0项，国家发明专利14项，请按您认为最具代表性、重要性或影响力的顺序列出：(不超过10项)

(填写格式：项目名称，奖励名称，奖励级别，授奖单位，获奖年月，本人排名/总人数)

3.5 任国际期刊编委、国际学术会议重要职务及在国际学术会议全会报告、特邀报告情况

3.6 获得专利情况

共获专利14项，其中发明专利14项。请按您认为最具代表性、重要性或影响力的顺序列出：（不超过10项）

(填写格式：专利名称，专利类型，专利授权国，专利号，授权公告年月，本人排名/总人数)

1. Metal cyanide complex catalyst, preparation method and uses thereof，美国发明专利，授权，US8859452，2014.10, 1/5.

2. 一种链结构规整的聚单硫代碳酸酯的制备方法 ，发明专利，授权，201310202810.0, 2015.05，1/4。

3. 一种用于碳酸二甲酯合成的催化剂的制备方法及应用，发明专利，授权，201210148342.9，2014.04，1/4。

4. 一种纳米结构环氧树脂固化物的制备方法和用途，发明专利，授权，201010225029.1，2012.03，1/3。

5. 一种链结构规整的脂肪族聚碳酸酯的合成方法，发明专利，授权， 201310035031.6，2015.02，1/3。

6. 一种双组分双金属催化剂的合成方法及应用，发明专利，授权， 201110428195.6，2015.04，1/4。

7. 含聚酯链节和聚碳酸酯链节的三元共聚物及其合成方法，发明专利，授权，200910098650.3，2011.05，1/3。

8. 主链和侧链均为碳-氧杂链结构的聚合物分子刷、合成方法，发明专利，授权，201110249714.2，2013.08，1/5。

9. 金属氰化物配位催化剂催化制备脂肪族聚碳酸酯的方法，发明专利，授权，201010253928.2，2012.05，1/5。

10. 一种金属氰化物配位催化剂及其制备方法和应用，发明专利，授权，201010253936.7，2012.05，1/5。

3.7 其他获奖及荣誉称号

1、发表在Polymer上的论文《Selective copolymerization of carbon dioxide with propylene oxide catalyzed by a nanolamellar double metal cyanide complex catalyst at low polymerization temperatures》（2011, 52(24), 5494-5502）获得2012年度冯新德最佳论文提名奖（ELSEVIER出版社）。

2、 2014年 《粘接》杂志，《非异氰酸酯路线合成聚羟氨酯的研究》在“中国胶粘剂行业首届优秀科技论文有奖征文大赛”中，获得“杰出奖”论文的荣誉。

3、
2013年浙江大学求是青年学者；
2012年浙江省自然科学学术奖三等奖，排名1；
2012年校级教学成果奖，排名5；
浙江大学2014年度院级先进工作者.

3.8 社会服务及兼职等

国家自然科学基金评审专家；浙江省自然科学基金通讯评议人。
国际期刊Macromolecules, Polym Chem, J Polym Sci Polym Chem, Polymer, Applied Catalysis A, Chemsubchem, Chem Comm, RSC adv, Dalton Trans和高分子学报等期刊审稿，年均30-40篇。
国际学术会议邀请口头报告3次和国内学术会议口头报告6次。
其它：
1）2007-2012级本科生班主任；
2）2012级新生之友；
3）指导6项浙江大学SRTP项目和浙江省大学生科技创新计划等本科生项目。
4）《高分子化学实验》教学改革；多次负责和参加高分子系研究生复试工作（实验）。
5）参加浙大本科生招生的安徽招生组。
6）高分子科学研究所副所长（2015年起），分管教学工作。

省教改项目的论文成果，8月份已被《高分子通报》接收，排版中。

四、 申请人主要学术成绩、贡献、创新点及其科学价值或社会经济意义(不超过3000字)

申请人研究方向是**催化与可控聚合**。主要集中于**催化C1单体(CO_2、COS和CS_2)与环氧化物共聚**的研究。以**锌−钴双金属氰化络合物(简称DMCC)**为对象，系统研究了DMCC制备及其催化C1单体与环氧化物共聚反应，发展了不同拓扑结构CO_2基共聚物的合成新方法，获得的新结构DMCC成为一种有重要应用前景的CO_2共聚催化剂。国家自然科学基金委化学部董建华研究员在《高分子通报》（2014，12，17-22）上发表的文章《高分子科学的几个重要研究方向与进展》中，指出了本小组近年在一碳单体聚合领域中所取得的重要进展。相关学术成绩、创新点和科学价值总结如下：

一、获得了基于Zn−OH键化学的非均相催化CO_2与环氧化物高效和选择性共聚的DMCC催化剂。

早期DMCC是环氧丙烷(PO)均聚的高效催化剂，用其催化CO_2/环氧化物共聚效率低、交替度不足50%，环状副产物含量达20wt%以上。以改造活性位点和增加比表面积来增强其吸附活化CO_2的能力为突破口，设计了双套溶胶−凝胶和模板诱导剥离法制备**新结构DMCC**催化剂，其新特征是：1) **活性位点为路易斯酸碱位于一体的Zn−OH键**，这类似于自然界中能高效活化空气中CO_2的碳酸酐锌酶的位点结构。基于此结构阐明了增长链向水等质子给体的链转移反应再生Zn−OH键的完整催化循环。2) **纳米片-孔或球-孔结构，反应压力下“爆破”为更小的颗粒**，显著增加了比表面积和裸露Zn−OH键数目。申请人报道的纳米片状DMCC催化剂，以水为溶剂制备，对空气和水不敏感，比表面积 >500 m^2/g，储存期长，可活化再生。该催化剂可在40-50 ºC催化CO_2/PO共聚，产物交替度可达74%。为实现CO_2/PO全交替共聚，基于表面吸附活化理论和PO插入为决速步的事实，通过向表面Zn−OH位点引入中性配体以构造位阻的局域环境，减小了PO连续插入的几率，由此得到的双组份DMCC，能高活性催化CO_2/PO全交替共聚，得到高分子量共聚物。相关结果已获授权发明专利3项(含1项美国专利，US8859452)。基于这一技术，目前与企业合作在建年产1万吨共聚物的生产线。

含**线形长烷基、支化烷基**和**含吸电子取代基**的端环氧化物与CO_2交替共聚的报道很少。尤其含吸电子基的端环氧化物与CO_2共聚时易偶合反应，需在室温甚至0 ºC及以下才能共聚，并需助催化剂协同作用。基于固相催化剂表面的吸附作用能改变反应途径、降低反应活化能的原理，纳米DMCC顺利催化了CO_2与上述环氧化物交替共聚，如其催化CO_2与氧化苯乙烯(SO)交替共聚、且仅在**次甲基**处选择性开环，在40−60 ºC下96 wt%的共聚产物是聚碳酸酯。而同样温度下采用(Salen)Co体系则主要生成环状产物。纳米DMCC能催化多种环氧单体与CO_2近全交替共聚，提供了玻璃化转变温度(T_g)从−44 ºC (CO_2/环氧十一烯酸甲酯全交替共聚物，是至今报道的最低T_g的CO_2基共聚物)到110 ºC [环氧环己烷(CHO)/CO_2共聚物]的系列CO_2基共聚物，因此，DMCC催化剂可用来制备生物降解型的塑料和弹性体，所得产物应用领域宽。同时也揭示了**环氧取代基的位阻效应决定交替度、电子效应决定区域选择性反应的重要规律**。相关结果发表在Polymer 2011, 52, 391; JPS part A, 2012, 50, 2924和Macromolecules, 2015, 48, 536等杂志上。

科学价值:

1) **通过纳米尺度内调控催化剂微观结构、确认活性位点和改造其配位环境来提高催化性能的方法，是研究非均相催化C1单体配位聚合的新思路**。制备组成确定的DMCC是揭示Zn−OH位点及其催化机制的前提，我们确证Zn−OH键及其催化机理的工作获得了同行的关注。如一直从事CO_2共聚研究的Donald J. Darensbourg教授在Angew Chem Int Ed 2013, 52, 10602-10606的文章中采用相同方法实现由金属-羟基键催化制备了双羟基聚碳酸酯，是在均相催化体系应用这一结果的扩展研究；Stephan Enthaler教授在综述文章ACS Catalysis 2013, 3, 150-158中指出我们的DMCC是锌类催化剂催化共聚的典型范例之一。

2) 基于上述Zn−OH键催化机理，**系统总结了新结构DMCC催化CO_2/环氧化物区域选择性共聚的规律和环氧单体结构效应**。如发表于Macromolecules 2013, 46, 3693-3697上关于纳米DMCC催化CO_2/SO交替共聚的体系，特点是区域选择反应仅由碳酸根阴离子和SO的苯基吸电子效应决定，这不同于均相金属络合物和有机碱协同作用的控制途径。吕小兵教授在Angew. Chem. Int. Ed. 2013, 52, 11594-11598和Macromolecules 2014, 47, 1269-1276中引用此文作为双金属协同配位催化CO_2/SO共聚的例子。

二、发展了结晶性多嵌段和刷状CO_2基共聚物的合成新方法。

申请人提出将结晶性的生物降解型聚合物如聚己内酯 (PCL)的链段有序引入至CO_2基共聚物中的思路，来解决CO_2基共聚物自身力学热学性能和生物降解性难以兼顾的不足，发展了两种合成新方法。一是基于**DMCC的Zn−OH键催化产生端羟基聚碳酸酯及其体系存在快速链转移**的事实，设想将CHO/CO_2共聚体系和同样存在快速链转移反应的己内酯开环聚合体系置于同一反应釜内，如两催化剂互不干扰，在交叉链交换反应能发生且低于平均链增长速率时，可能得到聚碳酸酯和聚酯段段交替的多嵌段共聚物。由此出发，一步合成得到了力学性能优异的结晶性多嵌段CO_2基共聚物 (Chemical Science, 2015, 6, 1530)。另一是精确合成了刷状CO_2基共聚物。以(Salen)Co配合物为模型催化剂，先合成窄分布的含有双键侧基的CO_2基共聚物，再由巯基-双键“点击”反应将侧基双键转化为羟基，然后接出PCL侧链，得到接枝率100%和侧链长度可调、结晶度可控的分子刷 (Macromolecules 2011, 44, 9882)。以DMCC

代替(Salen)Co催化剂，可高效率制得该类型分子刷。

科学价值:

在合成方法学上，**多嵌段CO_2基共聚物的合成是首例采用双催化剂催化三种不同类单体、经由不同机理一步制备多嵌段共聚物的范例**。而之前的方法均是基于同类催化剂和同样的催化机理。该工作在Chemical Science 2015, 6, 1530-1536发表后，在2015年第一个季度进入下载量最多的前25篇文章排行榜(http://blogs.rsc.org/sc/，下载1201次)。同行专家评价“张等报道的含PCHC和PCL段的多嵌段共聚物，是本领域内的显著进展，因为一些合成此类聚合物的尝试得到的是无规或有梯度结构的嵌段共聚物”。**刷状CO_2基共聚物的合成提供了一种非自由基可控聚合路线的精确合成方法**，如Charlotte K. Williams教授在Angew Chem Int Ed 2014, 53, 1607-1610中指出该工作是“三单体经由开环聚合和开环加聚分步合成共聚物仅有的几例报道之一[8,**11**]”，英国和澳大利亚皇家化学会会员Andrew B. Lowe教授在Polym Chem 2014, 5, 4820-4870中详细介绍了该工作(4841页和Scheme 2)。这一工作**也开启了侧羟基功能化CO_2基共聚物的研究**，如高分子合成化学家Holger Frey和Gerrit A. Luinstra教授分别在Macromolecules 2013, 46, 3280-3287和2014, 47, 492-497的论文中、Donald J. Darensbourg教授在Macromolecules 2014, 47, 3806-3813和7347-7353以及Polymer Chemistry 2015,6,1768-1776的论文中均引用了这一工作，报道了若干侧基功能化的CO_2基聚合物的合成。

三、开辟了催化含硫C1单体(CS_2和COS)与环氧化物选择性共聚的新领地。

基于含硫C1单体与CO_2结构相似、及碳酸酐锌酶的Zn−OH键定量转化CS_2为COS和CO_2的事实，申请人设想含Zn−OH键的DMCC可能催化CS_2或COS与环氧化物共聚。实验结果表明DMCC能高效催化CS_2/PO (CHO)共聚，重要的是发现了氧/硫原子交换反应和因此产生的多种中间产物单体交叉共聚的现象，得到聚多硫代碳酸酯，并提出了**氧/硫原子交换配位聚合的反应模式以及金属-羟基键导致氧/硫交换反应的假设**。基于这一设想，以(Salen)CrCl/有机碱体系催化COS与环氧化物，可高活性全交替共聚。在无水条件下，能完全抑制氧/硫原子交换反应。如引入水至聚合体系，则观察到Cr−OH键的生成及其诱发的氧/硫交换反应。这支持了之前金属-羟基键导致氧/硫交换反应的设想，也佐证了申请人提出的Zn-OH键催化CO_2共聚的机理。这些工作发表在Macromolecules 2013, 46, 5899; 2015, 48, 6057; 2015, 48, 5526; Polymer Chemistry, 2015, 6, 4978等杂志，形成较为系统的研究结果。

科学价值:

实现了催化含硫C1单体与环氧化物的共聚，得到了传统缩聚和开环聚合方法难以制得的新类型高折光指数的聚硫代碳酸酯。其学术价值在于：1) 发现了氧/硫交换反应，提供了开环加聚路线合成聚硫代碳酸酯的方法。2) 提出了二元不对称单体同时区域选择性开环加聚反应的加聚模式，建立了氧/硫交换反应的抑制方法。

五、其他能反映学术研究水平的突出业绩

无

个人承诺

本人保证：所从事的学术研究符合学术道德规范要求；所提供的材料客观真实。

承诺人：

年 月 日

上述材料均已审核，内容真实，与证明材料原件相符。

审核人：

年 月 日

Publication list:

2015

(1) Luo, M.; **Zhang, X.-H.***; Du, B.-Y.; Wang, Q.; Fan, Z.-Q. Well-defined high refractive index poly(monothiocarbonate) with tunable Abbe's numbers and glass-transition temperatures via terpolymerization. *Polymer Chemistry* **2015**, *6*, 4978-4983.

(2) Li, Y.; Hong, J.-L.; Wei, R.-J.; Zhang, Y.-Y.; Tong, Z.-Z.; **Zhang, X.-H.***; Du, B.-Y.; Xu, J.-T.; Fan, Z.-Q. Highly efficient one-pot/one-step synthesis of multiblock copolymers from three-component polymerization of carbon dioxide, epoxide and lactone. *Chemical Science* **2015**, *6*, 1530-1536.

(3) Zhang, Y.-Y.; Wei, R.-J.; **Zhang, X.-H.***; Du, B.-Y.; Fan, Z.-Q. Efficient solvent-free alternating copolymerization of CO_2 with 1, 2-epoxydodecane and terpolymerization with styrene oxide via heterogeneous catalysis. *Journal of Polymer Science Part A: Polymer Chemistry* **2015**, *53*, 737-744.

(4) Zhang, Y.-Y.; Li, Y.; Zhou, X.-J.; **Zhang, X.-H.***; Du, B.-Y.; Fan, Z.-Q. Synthesis of an Amphiphilic Brush Copolymer by a Highly Efficient “Grafting onto” Approach via CO_2 Chemistry. *Macromolecular Rapid Communications* **2015**, *36*, 852-857.

(5) **Zhang, X.-H.***; Wei, R.-J.; Zhang, Y.-Y.; Du, B.-Y.; Fan, Z.-Q. Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc–Cobalt(III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures. *Macromolecules* **2015**, *48*, 536-544.

(6) Min, Y.-Q.; Huang, S.-Y.; Wang, Y.-X.; Zhang, Z.-J.; Du, B.-Y.; **Zhang, X.-H.***; Fan, Z.-Q. Sonochemical Transformation of Epoxy–Amine Thermoset into Soluble and Reusable Polymers. *Macromolecules* **2015**, *48*, 316-322.

(7) Luo, M.; **Zhang, X.-H.***; Darensbourg, D. J. An Investigation of the Pathways for Oxygen/Sulfur Scramblings during the Copolymerization of Carbon Disulfide and Oxetane. *Macromolecules* **2015**, *48*, 5526-5532.

(8) Luo, M.; **Zhang, X.-H.***; Darensbourg, D. J. An Examination of the Steric and Electronic Effects in the Copolymerization of Carbonyl Sulfide and Styrene Oxide. *Macromolecules* **2015**, *48*, 6057-6062.

(9) Luo, M.; **Zhang, X. H.***; Darensbourg, D. J. Highly regioselective and alternating

copolymerization of carbonyl sulfide with phenyl glycidyl ether. *Polymer Chemistry* **2015**, *6*, 6955-6958.

(10) Luo, M.; **Zhang, X. H.***; Darensbourg, D. J. Synthesis of cyclic monothiocarbonates via the coupling reaction of carbonyl sulfide (COS) with epoxides. *Catalysis Science & Technology* **2015**. Advance Article. DOI: 10.1039/C5CY00977D

2014

(1) Luo, M.; **Zhang, X.-H.***; Du, B.-Y.; Wang, Q.; Fan, Z.-Q. Alternating copolymerization of carbonyl sulfide and Cyclohexene Oxide catalyzed by zinc–cobalt double metal cyanide complex. *Polymer* **2014**, *55*, 3688-3695.

(2) Wei, R.-J.; **Zhang, X.-H.***; Zhang, Y.-Y.; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Functional poly (carbonate-*co*-ether) synthesis from glycidyl methacrylate/CO_2 copolymerization catalyzed by Zn–Co (III) double metal cyanide complex catalyst. *RSC Advances* **2014**, *4*, 3188-3194.

(3) Wei, R.-J.; Zhang, Y.-Y.; **Zhang, X.-H.***; Du, B.-Y.; Fan, Z.-Q. Regio-selective synthesis of polyepichlorohydrin diol using Zn–Co (III) double metal cyanide complex. *RSC Advances* **2014**, *4*, 21765-21771.

(4) Zhang, Y.-Y.; **Zhang, X.-H.***; Wei, R.-J.; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Synthesis of fully alternating polycarbonate with low T_g from carbon dioxide and bio-based fatty acid. *RSC Advances* **2014**, *4*, 36183-36188.

(5) **Zhang, X.-H.***; Min, Y.-Q.; Hua, Z.-J. Epoxy-Based Electronic Materials Containing Nitrogen Heterocyclic Ring: Flame Retardancy. *Progress in chemistry* **2014**, *26*, 1021-1031.

(6) Hong, J.-L.; **Zhang, X.-H.***; Wei, R.-J.; Wang, Q.; Fan, Z.- Q.; Qi, G.-R. Inhibitory effect of hydrogen bonding on thermal decomposition of the nanocrystalline cellulose/poly (propylene carbonate) nanocomposite. *Journal of Applied Polymer Science* **2014**, *131*.

(7) Zhou, X.-J.; Zhou, Y.-Y.; Nie, J.-J.; Xu, J.-T.; **Zhang, X.-H.**; Du, B.-Y.* Thermosensitive Ionic Microgels via Surfactant-Free Emulsion Copolymerization and in Situ Quaternization Cross-Linking. *ACS Applied Materials & Interfaces* **2014**, *6*, 4498-4513.

(8) Chen, T.-Q.; Lu, Y.-P.; Chen, T.-Y.; **Zhang, X.-H.**; Du, B.-Y.* Adsorption of PNIPAm*x*-PEO_{20}-PPO_{70}-PEO_{20}-PNIPAm*x* pentablock terpolymer on gold surfaces: effects of concentration, temperature, block length, and surface properties. *Physical Chemistry Chemical Physics* **2014**, *16*, 5536-5544.

2013

(1) Wei, R.-J.; **Zhang, X.-H.***; Du, B.-Y.; Sun, X.-K.; Fan, Z.-Q.; Qi, G.-R. Highly Regioselective and Alternating Copolymerization of Racemic Styrene Oxide and Carbon Dioxide via Heterogeneous Double Metal Cyanide Complex Catalyst. *Macromolecules* **2013**, *46*, 3693-3697.

(2) Luo, M.; **Zhang, X.-H.***; Du, B.-Y.; Wang, Q.; Fan, Z.-Q. Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Racemic Propylene Oxide. *Macromolecules* **2013**, *46*, 5899-5904.

(3) Wei, R.-J.; **Zhang, X.-H.***; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Selective production of poly (carbonate–*co*–ether) over cyclic carbonate for epichlorohydrin and CO_2 copolymerization via heterogeneous catalysis of Zn–Co (III) double metal cyanide complex. *Polymer* **2013**, *54*, 6357-6362.

(4) Wei, R.-J.; **Zhang, X.-H.***; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Synthesis of bis (cyclic carbonate) and propylene carbonate via a one-pot coupling reaction of CO_2, bisepoxide and propylene oxide. *RSC Advances* **2013**, *3*, 17307-17313.

(5) Wei, R.-J.; **Zhang, X.-H.***; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Highly Active and Selective Binary Catalyst System for the Coupling Reaction of CO_2 and Hydrous Epoxides. *Journal of Molecular Catalysis A: Chemical* **2013**, *379*, 38-45.

(6) Lu, Y.-P.; Chen, T.-Q.; Mei, A.-X.; Chen, T.-Y.; Ding, Y.-W.; **Zhang, X.-H.**; Xu, J.-T.; Fan, Z.-Q.; Du, B.-Y.* Solution behaviors and microstructures of PNIPAm-P123-PNIPAm pentablock terpolymers in dilute and concentrated aqueous solutions. *Physical Chemistry Chemical Physics* **2013**, *15*, 8276-8286.

(7) Chen, T.-Y.; Du, B.-Y.*; **Zhang, X.-H.**; Fan, Z.-Q. Fabrication of Polymer Nanocapsules with Controllable Oligo (Ethylene Glycol) Densities, Permeation Properties and Robustly Crosslinked Walls. *ACS Applied Materials & Interfaces* **2013**, *5*, 3748-3756.

2012

(1) Sun, X.-K.; **Zhang, X.-H.***; Wei, R.-J.; Du, B.-Y.; Wang, Q.; Fan, Z.-Q.; Qi, G.-R. Mechanistic insight into initiation and chain transfer reaction of CO_2/cyclohexene oxide copolymerization catalyzed by zinc-cobalt double metal cyanide complex catalysts. *Journal of*

Polymer Science Part A: Polymer Chemistry **2012**, *50*, 2924-2934.

(2) Sun, X.-K.; Chen, S.; **Zhang, X.-H.***; Qi, G.-R. Double Metal Cyanide Complex Catalyst and Its Catalysis for Epoxides-Involved Polymerization. *Progress in Chemistry* **2012**, *24*, 1776-1784.

(3) Lu, Y.-P.; **Zhang, X.-H.**; Fan, Z.-Q.; Du, B.-Y.* Adsorption of $PNIPAm_{110}$-PEO_{100}-PPO_{65}-PEO_{100}-$PNIPAm_{110}$ pentablock terpolymer on hydrophobic gold. *Polymer* **2012**, *53*, 3791-3801.

2011

(1) Zhang, J.-F.; Ren, W.-M.; Sun, X.-K.; Meng, Y.; Du, B.-Y.; **Zhang, X.-H.*** Fully Degradable and Well-Defined Brush Copolymers from Combination of Living CO_2/Epoxide Copolymerization, Thiol–Ene Click Reaction and ROP of ε-caprolactone. *Macromolecules* **2011**, *44*, 9882-9886.

(2) **Zhang, X.-H.***; Wei, R.-J.; Sun, X.-K.; Zhang, J.-F.; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. Selective copolymerization of carbon dioxide with propylene oxide catalyzed by a nanolamellar double metal cyanide complex catalyst at low polymerization temperatures. *Polymer* **2011**, *52*, 5494-5502.

(3) Meng, Y.; **Zhang, X.-H.***; Du, B.-Y.; Zhou, B.-X.; Zhou, X.; Qi, G.-R. Thermosets with core–shell nanodomain by incorporation of core crosslinked star polymer into epoxy resin. *Polymer* **2011**, *52*, 391-399.

2010

(1) Sun, X.-K.; **Zhang, X.-H.***; Chen, S.; Du, B.-Y.; Wang, Q.; Fan, Z.-Q.; Qi, G.-R. One-pot terpolymerization of CO_2, cyclohexene oxide and maleic anhydride using a highly active heterogeneous double metal cyanide complex catalyst. *Polymer* **2010**, *51*, 5719-5725.

(2) Mei, A.-X.; Guo, X.-L.; Ding, Y.; **Zhang, X.-H.**; Xu, J.-T.; Fan, Z.-Q.; Du, B.-Y.* PNIPAm-PEO-PPO-PEO-PNIPAm pentablock terpolymer: synthesis and chain behavior in aqueous solution. *Macromolecules* **2010**, *43*, 7312-7320.

(3) Huang, Y.-J.; **Zhang, X.-H.***; Hua, Z.-J.; Chen, S.-L.; Qi, G.-R. Ring-Opening Polymerization of Propylene Oxide Catalyzed by a Calcium Chloride-Modified Zinc-Cobalt Double Metal-Cyanide Complex. *Macromolecular Chemistry and Physics* **2010**, *211*, 1229-1237.

2009

(1) Zhou, B.-X.; Huang, Y.-J.; **Zhang, X.-H.***; Fu, Z.-S.; Qi, G.-R. Thermal properties of an epoxy cresol-formaldehyde novolac/diaminodiphenyl sulfone system modified by bismaleimide containing tetramethylbiphenyl and aromatic ether structures. *Polymer Engineering & Science* **2009**, *49*, 1525-1532.

(2) **Zhang, X.-H.***; Zhou, B.-X.; Sun, X.-K.; Qi, G.-R. Cure kinetics and thermal properties of tetramethylbiphenyl epoxy resin/phthalazinone-containing diamine/hexa (phenoxy) cyclotriphophazene system. *Journal of Applied Polymer Science* **2009**, *114*, 1397-1404.

(3) Huang, Z.-Z.; **Zhang, X.-H.***; Qi, G.-R. Novel halogen-free flame retardant thermoset from a hybrid hexakis (methoxymethyl) melamine/phosphorus-containing epoxy resin cured with phenol formaldehyde novolac. *Express Polym. Lett* **2009**, *3*, 788-796.

(4) Du, B.-Y.*; Cao, Z.; Li, Z.-B.; Mei, A.-X.; **Zhang, X.-H.**; Nie, J.-J.; Xu, J.-T.; Fan, Z.-Q. One-Pot preparation of hollow silica spheres by using thermosensitive poly (N-isopropylacrylamide) as a reversible template. *Langmuir* **2009**, *25*, 12367-12373.

2008

(1) **Zhang, X.-H.***; Liu, F.; Sun, X.-K.; Chen, S.; Du, B.-Y.; Qi, G.-R.; Wan, K.-M. Atom-exchange coordination polymerization of carbon disulfide and propylene oxide by a highly effective double-metal cyanide complex. *Macromolecules* **2008**, *41*, 1587-1590.

(2) **Zhang, X.-H.***; Zhou, B.-X.; Sun, X.-K.; Qi, G.-R. Preparation and properties of epoxy/phenol formaldehyde novolac/hexakis (methoxymethyl) melamine hybrid resins from in situ polymerization. *Journal of Applied Polymer Science* **2008**, *110*, 4084-4092.

(3) Sun, X.-K.; **Zhang, X.-H.***; Liu, F.; Chen, S.; Du, B.-Y.; Wang, Q.; Fan, Z.-Q.; Qi, G.-R. Alternating copolymerization of carbon dioxide and cyclohexene oxide catalyzed by silicon dioxide/Zn-Co(III) double metal cyanide complex hybrid catalysts with a nanolamellar structure. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, *46*, 3128-3139.

2007

(1) **Zhang, X.-H.**; Hua, Z.-J.; Chen, S.; Liu, F.; Sun, X.-K.; Qi, G.-R.* Role of zinc chloride and complexing agents in highly active double metal cyanide catalysts for ring-opening

polymerization of propylene oxide. *Applied Catalysis A: General* **2007**, *325*, 91-98.

(2) **Zhang, X.-H.**; Liu, F.; Chen, S.; Qi, G.-R.* Novel flame retardant thermosets from nitrogen－containing and phosphorus-containing epoxy resins cured with dicyandiamide. *Journal of Applied Polymer Science* **2007**, *106*, 2391-2397.

(3) **Zhang, X.-H.**; Chen, S.; Wu, X.-M.; Sun, X.-K.; Liu, F.; Qi, G.-R.* Highly active double metal cyanide complexes: Effect of central metal and ligand on reaction of epoxide/CO$_2$. *Chinese Chemical Letters* **2007**, *18*, 887-890.

(4) **Zhang, X.-H.***; Huang, L.-H.; Chen, S.; Qi, G.-R. Improvement of thermal properties and flame retardancy of epoxy-amine thermosets by introducing bisphenol containing azomethine moiety. *eXPRESS Polymer Letters* **2007**, *1*, 326-332.

(5) **Zhang, X.-H.**; Chen, S.; Chen, T.; Sun, X.-K.; Liu, F.; Qi, G.-R.* Synthesis of a soluble azomethine－containing bisphenol and the properties of its modified epoxy thermosets. *Journal of Applied Polymer Science* **2007**, *106*, 1632-1639.

(6) Chen, S.; **Zhang, X.-H.**; Lin, F.; Qi, G.-R.* Preparation of double metal cyanide compleces from water-insoluble zinc compounds and their catalytic performance for copolymerization of epoxide and CO2. *Reaction Kinetics and Catalysis Letters* **2007**, *91*, 69-75.

2006

(1) **Zhang, X.-H.**; Chen, S.; Min, Y.-Q.; Qi, G.-R.* Synthesis of novel bisphenol containing phthalazinone and azomethine moieties and thermal properties of cured diamine/bisphenol/DGEBA polymers. *Polymer* **2006**, *47*, 1785-1795.

(2) **Zhang, X.-H.**; Min, Y.-Q.; Zhao, H.; Wan, H.-M.; Qi, G.-R.* Novel nitrogen-containing epoxy resin. II. Cure kinetics by differential scanning calorimetry. *Journal of Applied Polymer Science* **2006**, *100*, 3483-3489.

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Highly efficient one-pot/one-step synthesis of multiblock copolymers from three-component polymerization of carbon dioxide, epoxide and lactone†

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It is a long-standing challenge to combine mixed monomers into multiblock copolymer (MBC) in a one-pot/one-step polymerization manner. We report the first example of MBC with biodegradable polycarbonate and polyester blocks that were synthesized from highly efficient one-pot/one-step polymerization of cyclohexene oxide (CHO), CO_2 and ε-caprolactone (ε-CL) in the presence of zinc–cobalt double metal cyanide complex and stannous octoate. In this protocol, two cross-chain exchange reactions (CCER) occurred at dual catalysts respectively and connected two independent chain propagation procedures (*i.e.*, polycarbonate formation and polyester formation) simultaneously in a *block-by-block* manner, affording MBC without tapering structure. The multiblock structure of MBC was determined by the rate ratio of CCER to the two chain propagations and could be simply tuned by various kinetic factors. This protocol is also of significance due to partial utilization of renewable CO_2 and improved mechanical properties of the resultant MBC.

Introduction

The big concerns on the global energy and environmental issues prompt us to develop efficient methods to prepare new polymeric materials that can be derived from renewable resources. Aliphatic polycarbonates (APCs) and polyesters are two classes of biodegradable polymers with a bright future because of their practical advantages. APCs can be synthesized by copolymerization of epoxide with carbon dioxide (CO_2),[1] which is one of the most attractive renewable C1 resources and abundant, non-toxic and low-cost, while polyesters can be prepared by ring-opening polymerization of lactones[2] that can also be obtained from the renewable resources.[3] In contrast to the most of commercialized polycarbonates and polyesters *via* condensation polymerization, which requires long reaction time as well as high energy supply and releases small molecules as by-products, both CO_2/epoxide copolymerization and ring-opening polymerization of lactone are addition polymerizations and undergo a sustainable and environmentally benign process, which meets the principle of atom economy.

Another virtue of both ring-opening polymerization of lactone and CO_2/epoxide copolymerization is that they could be used to make CO_2-based di- and tri-block copolymers, which were rarely reported.[4–6] Generally, polycarbonate with one or two hydroxyl (–OH) end groups was at first synthesized by copolymerization of epoxide with CO_2 and then used as the macroinitiator for ring-opening polymerization of lactone. For example, Darensbourg and co-workers reported the syntheses of di- and tri-block copolymers from CO_2, epoxide and lactone *via* macroinitiator intermediate by tandem using a (Salen)Co(III) complex plus an organic base 1,8-diazabicyclo[5.4.0]undec-7-ene.[4] Williams *et al.* synthesized a di-block copolymer from epoxide, CO_2 and lactone by using a dizinc catalyst, which could be reversibly switched from a polycarbonate catalyst to a polyester catalyst by adding switching reagents.[5] These works elegantly provided di- and tri-block copolymers by multi-step or sequential operations. In this context, we present a one-pot/one-step synthesis of a new CO_2-based multiblock copolymer (MBC) without tapering from cyclohexene oxide (CHO), CO_2 and ε-caprolactone (ε-CL) *via* cross-chain exchange reaction (CCER) that bridged two independent chain propagations generated by two appropriately selected catalysts (Fig. 1) simultaneously.

CCER is a kind of chain-transfer reaction in which the propagating chain exchanged with a dormant chain with different structures. Indeed, many metal-catalyzed ring-opening polymerizations of lactone and CO_2/epoxide copolymerizations are chain-transfer polymerizations, namely, immortal

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† Electronic supplementary information (ESI) available: Text, figures and tables giving general experimental procedures and characterization data for multiblock copolymers. See DOI: 10.1039/c4sc03593c

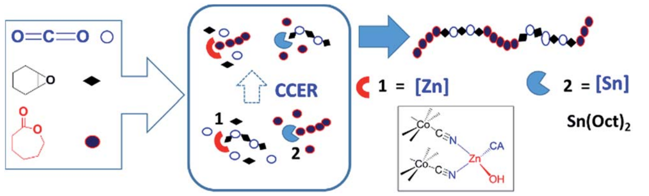
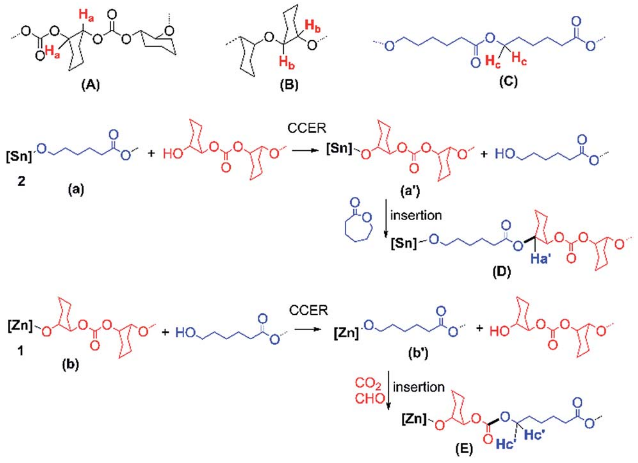


Fig. 1 Proposed cross-chain exchange polymerization of CO_2, CHO and ε-CL by using Zn–Co(III) DMCC (**1**, Scheme S1†)[7] and stannous octoate [**2**, Sn(Oct)$_2$] together.



Scheme 1 The main units (**A**–**C**), CCERs and the possible junction units of (**D**) and (**E**) in MBCs.

polymerization.[7,8] In such mode, a propagating chain could be converted to a dormant chain with at least one hydroxyl end group (macromolecular chain-transfer agent) *via* chain-transfer reaction to the proton compounds (*e.g.*, trace water) with much higher rate than those of the chain propagations.[7] The generated dormant chains could participate in the chain propagation again as macromolecular chain-transfer agents.[2,7,8] Therefore, it was possible to produce MBC by bridging CO_2/epoxide copolymerization and ring-opening polymerization of lactone *via in situ* generation of macromolecular chain-transfer agents during terpolymerization of CHO, CO_2 and ε-CL in one reactor.

Results and discussion

To this end, two catalysts, zinc–cobalt double metal cyanide complex (Zn–Co(III) DMCC, **1**) and stannous octoate [Sn(Oct)$_2$, **2**], were screened out (Fig. 1).[9] A nanolamellar Zn–Co(III) DMCC [Fig. S1, its synthesis and characterization are given in the ESI†] is a highly active catalyst for CO_2/epoxide copolymerization without producing the byproduct of cyclic carbonate at 50–110 °C.[7,10] The initiating site of **1** is zinc–hydroxyl group (Zn–OH, Scheme S1†), which could afford poly(cyclohexene carbonate) with two hydroxyl end groups (HO–PCHC–OH) resulted from Zn–OH initiation and chain-transfer reaction, respectively.[7] **2**-Catalyzed ring-opening polymerization of ε-CL is a typical chain-transfer polymerization at *ca.* 80–130 °C.[11] When CO_2/CHO copolymerization and ring-opening polymerization of ε-CL were combined into one reactor in the presence of **1** and **2** simultaneously, CCER would occur, as shown in Scheme 1, when the dormant polycarbonate exchanged with (**a**), a new propagating species (**a′**) was generated so that polycaprolactone (PCL) block was produced *via* consecutive ε-CL insertion and a junction unit **D** was formed. Thermodynamically, the insertion of ε-CL into (**a′**) made the equilibrium reaction to the right hand. Similarly, a propagating species (**b′**) would be generated *via* CCER along with the formation of PCHC block and the junction unit **E**. Hence, the resulted MBC would have the main units (**A** and **C**) and new junction units **D** and **E**. The production of the ether unit (**B**) was minor due to the catalytic behavior of Zn–Co(III) DMCC for CO_2/CHO copolymerization according to our previous report.[7]

The prerequisite for the formation of MBC is that **1**-catalyzed CO_2/CHO copolymerization and **2**-catalyzed ring-opening polymerization of ε-CL could occur independently with matched polymerization rates. The control experiments indicated that **1** was completely inactive to ring-opening polymerization of ε-CL in the presence or absence of CO_2 (Table S3, runs S1 and S2†). When **1** was used for CHO, CO_2 and ε-CL (Table S3, run-S3†), only PCHC with fully alternating structure was obtained (Fig. S2†), indicating the complete inhibition of CHO/ε-CL copolymerization in this case. **2** Failed to catalyze either CHO/CO_2 copolymerization or ring-opening polymerization of CHO (Table S3, runs S4 and S5†). When **2** was used for CHO and ε-CL in the presence or absence of CO_2 (Table S3, runs S6 and S7†), only PCL was obtained. Therefore, the crossed polymerization of three monomers with either catalysts **1** or **2** was kinetically precluded. CO_2 self-polymerization and CO_2/ε-CL copolymerization were also thermodynamically inhibited.[1] Furthermore, **1** could catalyze CHO/CO_2 copolymerization independently in the presence of **2**, *vice versa* (Table S3, runs S8 and S9†) with close-up monomer conversions (CHO: 95%; ε-CL: 86%), indicating that both CHO/CO_2 copolymerization and ring-opening polymerization of ε-CL could proceed independently with matched polymerization rates.

A series of one-pot polymerizations with mixed monomers of CHO, CO_2 and ε-CL in the presence of **1** and **2** were carried out (runs 3–6, Table 1) under mechanical stirring with 500 rpm. GPC results showed that the resultant MBCs had single elution curves (Fig. 2) with PDIs of 1.8–2.0. The number-average molecular weights (M_n) increased from 9.7 to 35.2 kg mol^{-1} with decreasing the [BnOH]/[ε-CL] molar ratios from 1 : 40 to 0. Note that BnOH could initiate ring-opening polymerization of ε-CL[8] and be used to tune the molecular weights of the resultant MBCs. 97–99% CHO and 94–96% ε-CL were converted within 4.0 h according to the ^{1}H NMR spectra of the crude products, indicating that two catalysts presented high efficiency towards this terpolymerization. Moreover, the ether units of MBCs obtained at 100 °C were dramatically inhibited (3.4–9.9% for runs 3–5 in Table 1) in contrast to the pure PCHC with the ether unit of 19.0% (run-1, Table 1, bulk polymerization). This could be attributed to the solvent-assisted depression effect (herein, ε-CL).[12] With such small

Table 1 Results of CHO/CO_2 copolymerization, ring-opening polymerization of ε-CL and CHO/CO_2/ε-CL terpolymerization[a]

Run	[OH]/[ε-CL]	M_n/PDI[b] kg mol^{-1}	Composition[c] (%) C	A	B	N[d]	Conv.[e] (%) CHO/ε-CL
1[f]	—	29.9/1.8	—	81.0	19.0	—	99/—
2[g]	1 : 150	22.7/1.7	100	—	—	—	—/84
3	1 : 40	9.7/2.0	52.1	38.1	9.9	10	97/94
4	1 : 150	18.7/1.8	49.5	46.6	3.9	9	99/95
5	0	35.2/1.9	49.2	47.5	3.4	3	98/96
6[h]	1 : 125	14.9/3.7	50.2	40.4	9.4	10	99/92

[a] Reaction conditions of runs 3–5: 100 °C, 4.0 MPa, 35.0 mg of **1**, [OH]/[**2**] = 2/1, 4.0 h, 30.0 mL CHO, 30.0 mL ε-CL, 20.0 mL THF, [OH] was benzyl alcohol (BnOH) for ring-opening polymerization of ε-CL. [b] Determined by gel permeation chromatography (GPC) of the purified product calibrated with polystyrene standards in THF. [c] Determined by ^{1}H NMR spectroscopy, **C** (polyester) = $A_{2.31}/(A_{4.67} + A_{3.2-3.5} + A_{2.31})$, **A** (polycarbonate) = $A_{4.67}/(A_{4.67} + A_{3.2-3.5} + A_{2.31})$, **B** (polyether) = $A_{3.2-3.5}/(A_{4.67} + A_{3.2-3.5} + A_{2.31})$. [d] Determined by ^{1}H NMR spectroscopy, $N = (2A_{4.79} + A_{4.13})/(A_{4.79} + A_{4.67} + A_{4.50} + A_{3.2-3.5} + A_{2.31})$ (see Fig. S3). [e] Based on ^{1}H NMR spectroscopy of the crude products. [f] Bulk. [g] In a flask under magnetic stirring. [h] Pentaerythritol, [pentaerythritol]/[ε-CL] = 1/500, 2.0 MPa CO_2 pressure.

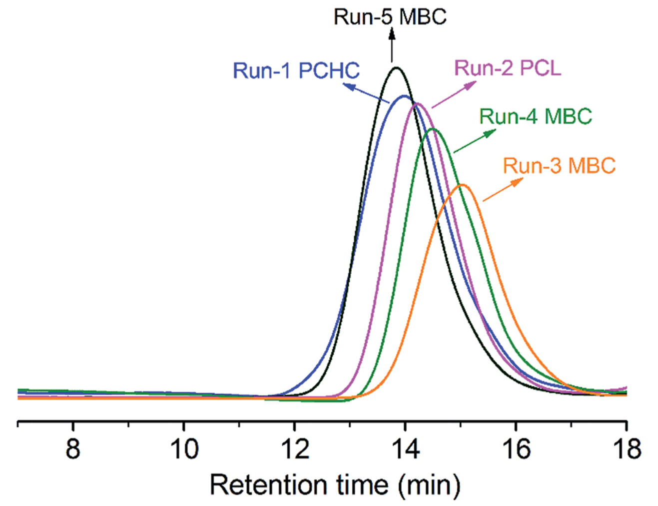


Fig. 2 GPC traces of the purified PCHC, PCL and the resultant terpolymers from runs 1–5 in Table 1.

amounts of the ether units in PCHC block, the possible junction units linked with consecutive ether units could be literally minimized (Schemes S2 and S3†).

The junction units **D** and **E** between PCHC and PCL blocks were confirmed by ^{1}H (^{13}C) NMR spectra of the resultant MBCs (Fig. 3-A and S4†). In contrast to the ^{1}H NMR spectra of PCL and PCHC, two small shoulder peaks at 4.12 and 4.79 ppm were clearly observed in Fig. 3-A. Both peaks could be ascribed to the proton signals of **E** (H_c') and **D** (H_a') respectively. Fig. 3-B shows the high-resolution ^{1}H–^{13}C heteronuclear single-quantum coherence (HSQC) spectrum of the run-3 MBC in Table 1. Both H_c' of **E** (4.11 ppm) and H_a' of **D** (4.78 ppm) in the ^{1}H NMR spectrum were directly correlated to the carbon of carbonate unit (67.70 ppm) and the ester unit (73.25 ppm) in ^{13}C NMR spectrum, respectively. In comparison, ^{1}H–^{13}C HSQC spectrum (Fig. S5-C†) of the PCHC/PCL blend (weight ratio of 1/1), which was prepared by using two catalysts under 100 °C and 4.0 MPa CO_2 pressure for 4 h in the autoclave, showed no junction units. As a result, no transesterification between PCHC and PCL occurred during terpolymerization.

Furthermore, CCERs with two catalysts were clearly disclosed by the observation that two junction units **E** and **D** were produced at Zn and Sn sites, respectively. Firstly, HO–PCL–OH

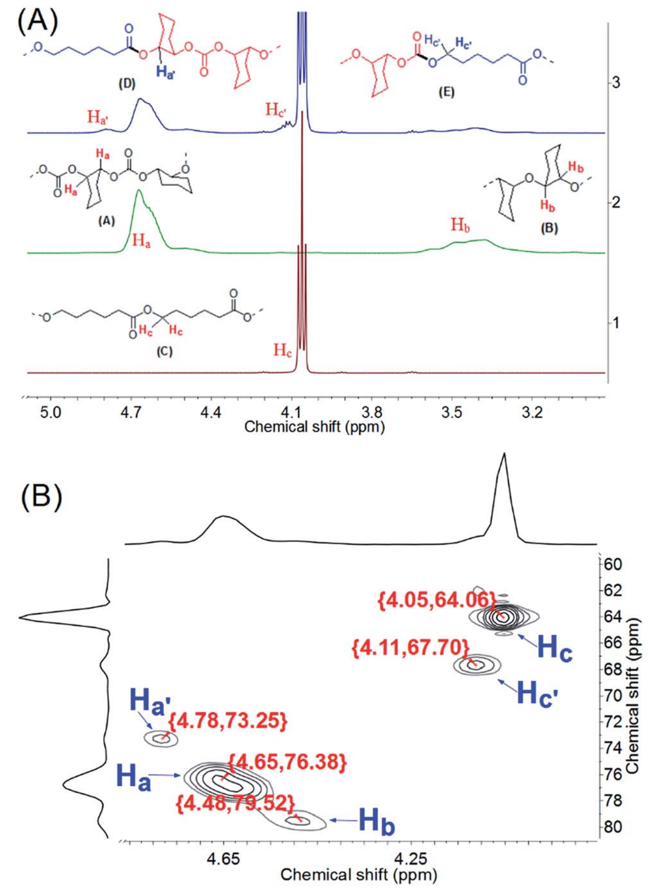


Fig. 3 (A) ^{1}H NMR results (500 MHz, $CDCl_3$) of PCL, PCHC and the run-3 terpolymer in Table 1 (spectra 1, 2 and 3 respectively), ^{1}H NMR test with rotating the tube was performed for the run-3 terpolymer; (B) ^{1}H–^{13}C HSQC spectrum (500 MHz NMR instrument) of the run-3 terpolymer in Table 1.

with a M_n of 1700 (run-S10 in Table S3 and Fig. S6†) was introduced into the **1**-catalyzed CO_2/CHO copolymerization system; the ^1H–^{13}C HSQC NMR spectrum of the resultant polymers (Fig. S5-D†) showed only one junction unit **E** {4.12 ppm, 67.83 ppm}, which was solely caused by the chain exchange reaction of HO–PCL–OH on Zn site. Moreover, when HO–PCHC–OH with a M_n of 700 was introduced into the **2**-catalyzed ring-opening polymerization of ε-CL system under 4.0 MPa CO_2 pressure (run-S11 in Table S3 and Fig. S6†), ^1H–^{13}C HSQC NMR spectrum of the product showed only one junction unit **D** {4.80, 73.52 ppm} (Fig. S5-E†). This result confirmed that the CCER only occurred on the Sn site.

In order to form multiblocks, the total rates of two CCERs should be smaller than those of corresponding propagation processes. The rate percentage of two CCERs to two propagations (N) could be estimated by the ratio of the integral area of **D** and **E** to the total carbonate (including small amounts of ether unit) and ester units based on ^1H NMR spectra. N of runs 3–5 MBCs in Table 1 was calculated to be *ca.* 3–10%, indicating that the total formation rate of the junction units **D** and **E** were *ca.* 3–10% of the MBC formation. Such rate difference between CCER and chain propagations led to the formation of polycarbonate and polyester multiblocks. Moreover, the rate ratio of **D** formation to the polycarbonate formation was approximately equal to that of **E** formation to the polyester formation based on the ^1H NMR spectra (Fig. S3†), suggesting that CCERs at the Zn and Sn site had nearly the same reactivity.

The evolution of the block structure of MBC was further monitored by the apparent kinetic study of the terpolymerization (Fig. 4 and S7–S10 and Table S4†). Fig. 4 shows the semilogarithmic plots of the conversions of CHO and ε-CL (Table S4†) *vs.* the reaction time with the assumption of the first-order dependence on monomer concentration for two polymerizations. The rate ratio of CHO/CO_2 copolymerization to ring-opening polymerization of ε-CL was estimated to be *ca.* 3, suggesting that the rate constant of CHO/CO_2 copolymerization was three times than that of ring-opening polymerization of ε-CL. As a result, the average block length of PCHC block was longer than that of PCL block in the resultant MBC. The ratio of the integral area of the junction units (**D** + **E**) to the total units (**A** + **C** + **B**) of MBC in ^1H NMR spectrum kept in the range of 11–14% (Table S4†) in the whole polymerization time, which ensured the continuous production of multiblocks at nearly stable rate. Moreover, M_n increased with the conversion of CHO and ε-CL in a nearly linear manner (Fig. S9†). In this sense, the obtained MBCs are statistical multiblock copolymers.

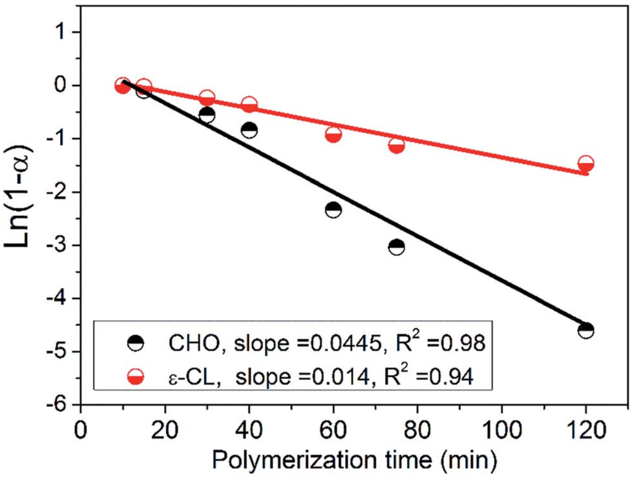


Fig. 4 Plots of ln(1 − α) *vs.* reaction time for the conversion (α) of CHO, ε-CL during terpolymerization with the assumption of the first-order dependence on the monomer concentration: [**2**]/[BnOH]/[ε-CL] = 0.5/1/40; 101 ± 2 °C (*ca.* 20–120 min), 4.0 MPa CO_2 pressure.

There are only a few examples of MBC synthesized by using two catalysts.[13,14] In the previous reports, two catalysts of the same type were used to catalyze two monomers with same functionality (*e.g.*, double bond)[13] or one monomer with R and S enantiomers.[14] In these cases, the transition of one block to another *via* chain shuttling obeyed the same propagation manner, which might cause tapering structure in the resultant multiblock copolymers. Our example reported in the present work provides a novel CCER route between two independent chain propagation processes catalyzed by two different types of catalysts for three monomers with different functionalities in a one-pot/one-step way, affording MBCs without tapering.

The multiblock structure of MBCs was also evidenced by the differential scanning calorimetry (DSC) results of the runs 3–5 MBCs from Table 1 with heating and cooling rates of 20 °C min^{-1} (Fig. 5) and 10 °C min^{-1} (Fig. S11†). As shown in Fig. 5-A, the melting temperatures (T_m) of the PCL block of runs 3–5 MBCs were observed (all samples were kept at 0 °C for at least 24 h before testing and complete crystallization). Since MBC with smaller N had a longer average block length, T_m values of runs 3–5 MBCs increased from 45.7 to 54.2 °C with decreasing N value and were lower than that of the PCHC/PCL blend (58.8 °C, Fig. 5-A). T_g values of run-5 and run-4 MBCs were found to be 79.3 and 71.8 °C (see inserted chart in Fig. 5-A), respectively. Both were lower than that of the PCL/PCHC blend (115.0 °C). However, no T_g was observed for the run-3 MBC (Fig. 5-A), in which the glass transition of the run-3 MBC might be neutralized by the melting process with strong enthalpy of the PCL block.

Subsequent DSC measurements were further carried out for the samples with heat treatment at 160 °C for 10 min. As shown in Fig. 5-B, the cooling curves of the PCL/PCHC blend and run-5 MBC presented crystallization temperatures (T_c) at 29.4 and 5.5 °C, and T_g at 117.3 and 80.0 °C, respectively. The low T_c of run-5 MBC was caused by the restricted crystallization of PCL blocks, which are covalently linked with PCHC blocks, with relatively high T_g.[15] However, no T_c and T_m were observed for runs 3–4 MBCs. The disappearance of crystallization and melting peaks in the rapidly cooled runs 3–4 MBCs suggested that the crystallization rate of these two samples was very slow. This is also one of the characteristics of restricted crystallization, which is frequently observed in semicrystalline block copolymers.[15] T_g values of runs 3–4 MBCs could be observed at *ca.* 69.0 °C when their DSC curves were magnified and the base line subtracted (Fig. S12†). It is reasonable that both MBCs had nearly the same chain compositions (Table 1). Moreover, when

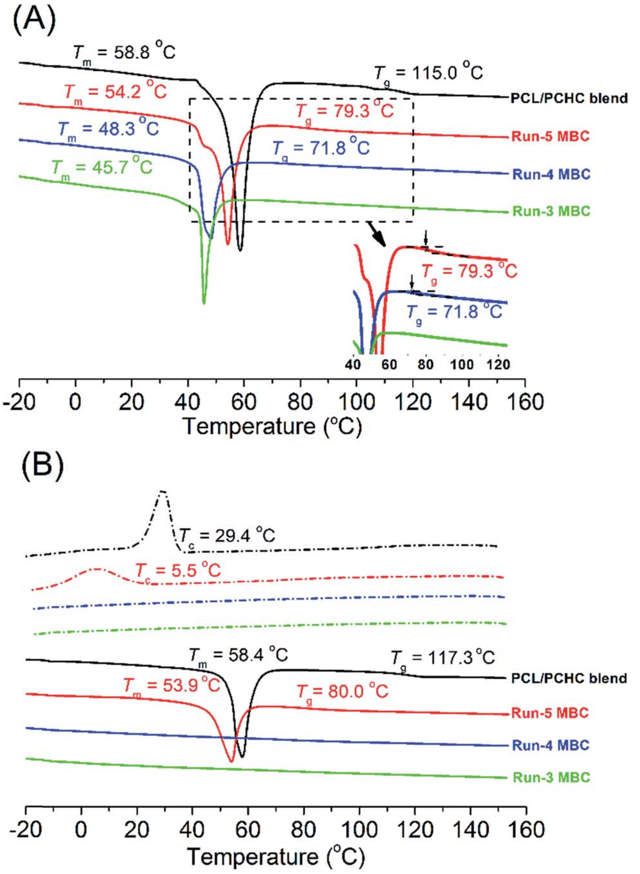


Fig. 5 DSC traces of MBCs from runs 3–5 in Table 1 and PCL/PCHC blend (M_n: 26.4 kg mol^{-1}) obtained with a heating rate of 20 °C min^{-1} in N_2 atmosphere, *ca.* 10 mg sample was used. The curves were shifted vertically for clarity. (A) Samples were kept at 0 °C for at least 24 h before testing for complete crystallization, samples were then heated from −20 to 160 °C; (B) the same samples were kept at 160 °C for 10 min, then were cooled to −20 °C and heated to 160 °C again.

DSC measurement was carried out for runs 3–5 and the PCL/PCHC blend with a heating and cooling rate of 10 °C min^{-1}, T_c and T_m values of the sample were similar with those in Fig. 5 (Fig. S11†). The above DSC results confirmed the production of multiblock structure of MBCs *via* one-pot/one-step reaction of three monomers catalyzed by two different catalysts.

The restricted crystallization behavior of PCL blocks in MBCs was also confirmed by the comparative study of small-angle X-ray scattering (SAXS) profiles of run-5 MBC in Table 1 and PCL/PCHC blend. As seen in Fig. 6-A, run-5 MBC presented a lamellar crystal thickness (l_c) of 3.4 nm, which was smaller than that of PCL/PCHC blend (4.6 nm). Due to the multiblock structure, the run-5 MBC in Table 1 showed improved elongation at break of 22.8% relative to those of PCHC (3.3%)[16] and PCHC/PCL blend (1.8%) (Fig. 6-B), which meant that the run-5 MBC was tougher than the pure PCHC and PCHC/PCL blend.

We also examined the effect of CO_2 pressure, CHO/ε-CL feeding ratio, reaction temperature, the type as well as the amount of the initiator on the structure of the resultant MBCs (Tables 1, S6 and S7†). With the fixed molar ratios of **1** to CHO and **2** to ε-CL, the variation of CHO/ε-CL ratio had a strong impact on the chain composition of the resultant polymers. When CHO/ε-CL volume ratio was 1/4 (run-S26 in Table S7†), an MBC with shorter PCHC block was obtained with a T_m of 56.9 °C that was less than that of the PCL/PCHC blend (58.4 °C,

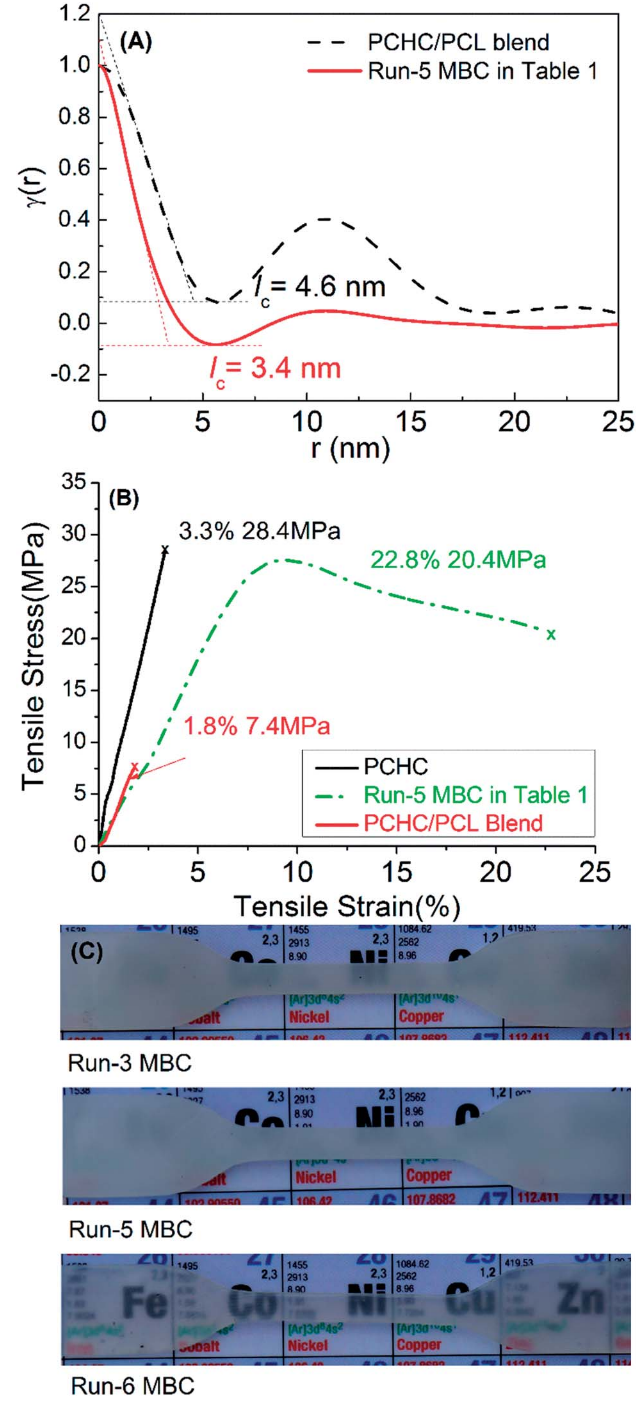


Fig. 6 (A) SAXS results: one-dimensional correlation functions for run-5 MBC in Table 1 (solid line) and the PCL/PCHC blend (dashed line); (B) stress–strain curves of run-5 MBC in Table 1, PCL/PCHC blend and PCHC (M_n: 37.4 kg mol^{-1}) at room temperature and 10 mm min^{-1}, * denotes failure point. (C) Images of run-3, run-5 and run-6 MBCs (dog bone sample, thickness of 2.0 mm) in Table 1 synthesized under different conditions.

Fig. S13†), indicating that even very short PCHC blocks in MBC could result in restricted crystallization of the PCL block. The suitable temperatures and CO_2 pressure for synthesizing MBCs were 90–110 °C and ≥2.0 MPa, respectively. PCL block in MBCs in Table S6† kept nearly in the range of 44.7–51.9%. Remarkably, the average block lengths of MBCs could be tuned by changing the type and amounts of the initiator. MBCs from run-3 and run-5 (thickness of 2.0 mm, Table 1) were semi-transparent and non-transparent, respectively (Fig. 6-C). Larger amount of initiator caused shorter average block lengths, which formed relatively thinner PCL lamellar crystals in the sample. When pentaerythritol was used as the initiator (run-6, Table 1), soft and transparent sample was obtained, suggesting that the crystallization of PCL blocks in the armed MBCs was more severely restricted.

Conclusions

In summary, we described a convenient method to synthesize MBCs with high efficiency from a one-pot/one-step polymerization of CO_2, CHO and ε-CL by bridging two independent chain propagations *via* CCER in one system. This reaction is also of significance because it produced multiblock copolymers without tapering by partially using renewable CO_2. Such MBCs with improved mechanical properties have a CO_2 uptake up to 15 mol% when [CHO]/[ε-CL] feeding ratio was 1.0. The ongoing work will be directed towards MBCs with tunable properties by precise kinetic control.

Experimental

Typical terpolymerization of CHO, CO_2 and ε-CL in a one-pot/one-step procedure: the terpolymerization was conducted in a Büchi autoclave, which had been pre-dried at 80 °C under vacuum for 2 h. Desired amounts of Zn–Co(III) DMCC, $Sn(Oct)_2$ (in dried THF), BnOH, CHO and ε-CL were transferred into the autoclave equipped with a mechanical stirrer (500 rpm) and a pressure gauge, CO_2 was then pressurized to the target pressure. The autoclave was heated by a cyclic oil heating bath with designed temperature (*e.g.*, 100 °C) and kept stirring for a certain time (*e.g.*, 4 h). After reaction, the autoclave was cooled down to room temperature and CO_2 was slowly vented. A small amount of the crude product was taken out for ^1H NMR measurement. The remaining sample was dissolved in CH_2Cl_2 and precipitated from methanol. This process was repeated three times to give the purified polymers.

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Notes and references

1 (*a*) S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287; (*b*) D. J. Darensbourg and M. W. Holtcamp, *Coord. Chem. Rev.*, 1996, **153**, 155; (*c*) G. W. Coates and D. R. Moore, *Angew. Chem., Int. Ed.*, 2004, **43**, 6618; (*d*) D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps and D. R. Billodeaux, *Acc. Chem. Res.*, 2004, **37**, 836; (*e*) H. Sugimoto and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 5561; (*f*) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388; (*g*) S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460; (*h*) M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141; (*i*) X.-B. Lu, W.-M. Ren and G.-P. Wu, *Acc. Chem. Res.*, 2012, **45**, 1721; (*j*) X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462.

2 (*a*) M. Labet and W. Thielemans, *Chem. Soc. Rev.*, 2009, **38**, 3484; (*b*) R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11; (*c*) C. K. Williams and M. A. Hillmyer, *Polym. Rev.*, 2008, **48**, 1; (*d*) M. H. Chisholm and Z. P. Zhou, *J. Mater. Chem.*, 2004, **14**, 3081; (*e*) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.

3 (*a*) R. R. A. Kitson, A. Millemaggi and R. J. K. Taylor, *Angew. Chem., Int. Ed.*, 2009, **48**, 9426; (*b*) H. Miao and E. Y.-X. Chen, *Macromolecules*, 2014, **47**, 3614.

4 (*a*) G.-P. Wu, D. J. Darensbourg and X.-B. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 17739; (*b*) D. J. Darensbourg and G.-P. Wu, *Angew. Chem., Int. Ed.*, 2013, **52**, 10602.

5 (*a*) M. R. Kember, J. Copley, A. Buchard and C. K. Williams, *Polym. Chem.*, 2012, **3**, 1196; (*b*) C. Romain and C. K. Williams, *Angew. Chem., Int. Ed.*, 2014, **53**, 1607; (*c*) M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676.

6 J.-F. Zhang, W.-M. Ren, X.-K. Sun, Y. Meng, B.-Y. Du and X.-H. Zhang, *Macromolecules*, 2011, **44**, 9882.

7 X.-K. Sun, X.-H. Zhang, R.-J. Wei, B.-Y. Du, Q. Wang, Z.-Q. Fan and G.-R. Qi, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2924.

8 (*a*) S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2861; (*b*) A. Cyriac, S. H. Lee, J. K. Varghese, E. S. Park, J. H. Park and B. Y. Lee, *Macromolecules*, 2010, **43**, 7398.

9 Catalyst pairs of (Salen)Co(or Cr) complexes/$Sn(Oct)_2$(PPNCl, TBD and DBU) and zinc glutarate/$Sn(Oct)_2$, were applied to the terpolymerization of CO_2, CHO and ε-CL, but failed to produce MBCs because of the unmatched polymerization rates, and poisoning of catalysts.

10 X.-K. Sun, X.-H. Zhang, F. Liu, S. Chen, B.-Y. Du, Q. Wang, Z.-Q. Fan and G.-R. Qi, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 3128.

11 (*a*) A. Duda, *Macromolecules*, 1994, **27**, 576; (*b*) M. R. Dorn, J. D. Lennon, G. L. Glish and M. R. Gagné, *Macromolecules*, 1999, **32**, 5149; (*c*) A. Kowalski, J. Libiszowski, T. Biela, M. Cypryk, A. Duda and S. Penczek, *Macromolecules*, 2005, **38**, 8170; (*d*) R. F. Storey and J. W. Sherman, *Macromolecules*, 2002, **35**, 1504.

12 X.-K. Sun, X.-H. Zhang, S. Chen, B.-Y. Du, Q. Wang, Z.-Q. Fan and G.-R. Qi, *Polymer*, 2010, **51**, 5719.

13 D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman and T. T. Wenzel, *Science*, 2006, **312**, 714.

14 W. Zhao, Y. Wang, X.-L. Liu, X.-S. Chen, D.-M. Cui and E. Y.-X. Chen, *Chem. Commun.*, 2012, **48**, 6375.

15 Z.-Z. Tong, B. Zhou, J. Huang, J.-T. Xu and Z.-Q. Fan, *Macromolecules*, 2014, **47**, 333.

16 C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steeman and D. J. Darensbourg, *Polymer*, 2001, **42**, 3995.

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Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc–Cobalt(III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures

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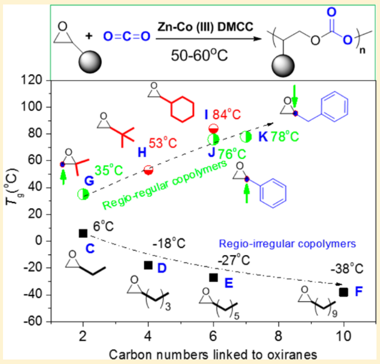
Ⓢ *Supporting Information*



ABSTRACT: In this study, we describe the substituent effect of epoxides on CO_2/epoxide copolymerization catalyzed by a nanosized zinc–cobalt(III) double metal cyanide complex [Zn–Co(III) DMCC]. The Zn–Co(III) DMCC catalyzed the copolymerization of CO_2 with 11 epoxides with alkyl or aryl groups at 50–60 °C within 15 h. The reaction afforded various CO_2/epoxide copolymers with high epoxide conversion efficiencies up to 100%. The alternating degree (F_{CO_2}) of the resulting copolymer was solely decided by the steric hindrance of the substituents of the epoxides regardless of their electron-donating or withdrawing properties. Substituents with large steric hindrances (2, 2-dimethyl, *tert*-butyl, cyclohexyl, decyl, and benzyl) led to highly alternating degrees (up to 100%). The regioselective CO_2/epoxide copolymerization was dominated by the electron induction effect of the substituent. The electron-withdrawing substituent such as phenyl and benzyl induced regioselective ring-opening at the methine site of the epoxide. For CO_2/isobutene oxide copolymerization, the regioselective reaction occurred at the methylene site of the isobutene oxide because of the strong electron-donating ability and steric hindrance of the two methyls of the isobutene oxide. The linear alkyl groups of the epoxides could not induce the regioselective reaction during copolymerization. The glass transition temperatures (T_gs) of the CO_2/epoxide copolymers with linear alkyl substituent groups decreased from +6 to −38 °C with increasing alkyl length, but increased from 6 to 84 °C with increasing steric hindrance of the epoxide substituents. Thus, various CO_2/epoxide copolymers with a wide T_g range from −38 to +84 °C were provided and could be applied as elastomers or plastics.

■ INTRODUCTION

Transforming carbon dioxide (CO_2) into polymeric materials by alternating copolymerization of CO_2 with epoxides is incredibly promising. Since the pioneering work of CO_2/propylene oxide (PO) copolymerization catalyzed by $ZnEt_2/H_2O$ system reported by Inoue et al. in 1969,[1] tremendous advances have been made in this field.[2−6] Indeed, CO_2/PO copolymer has been commercialized and shows a bright future for CO_2-based polymeric materials,[7,8] which encouraged us to expand the application of CO_2/epoxide copolymers into the area of plastics or elastomers. Thus, it is a necessity to design and synthesize CO_2/epoxide copolymers with various glass transition temperatures (T_gs) across a wide temperature range. Epoxides with different substituents offer many opportunities to synthesize CO_2/epoxide copolymers with various T_gs; however, the substituent effects of the epoxide on CO_2/epoxide copolymerization (polycarbonate selectivity, regioselectivity and glass transition temperatures) have not yet been systematically investigated.

The copolymerization of CO_2 with the epoxides containing long linear alkyl groups could create copolymers with T_gs below room temperature.[9−11] Such CO_2/epoxide copolymers with low T_g could serve as biodegradable elastomers—a new application of CO_2-based polymers.[8a,c] However, the copolymerization of CO_2 with epoxides containing long linear alkyl groups have rarely been reported likely because of the relatively low reactivity of these epoxides. Coates and co-workers reported CO_2/1,2-butene oxide copolymerization using a zinc β-diiminate complex catalyst at 25 °C and 300 psi CO_2. This produced 15% cyclic carbonate.[9] The turnover frequency (TOF) of this copolymerization had <50% the activity of CO_2/PO copolymerization with the same catalyst. The alternating copolymerization of 1, 2-butene oxide, 1,2-hexene oxide and 1,2-octene oxide with CO_2 were reported by the Lu group using a (Salen)Co(III) complex with (PPN)Cl, [bis(triphenylphosphine)iminium] chloride, at 25–40 °C for 3–4 h. This gave copolymers with polycarbonate selectivity of 97–99%,[10] while the TOFs of these copolymerizations also decreased dramatically versus the CO_2/PO copolymerization with the same catalyst.

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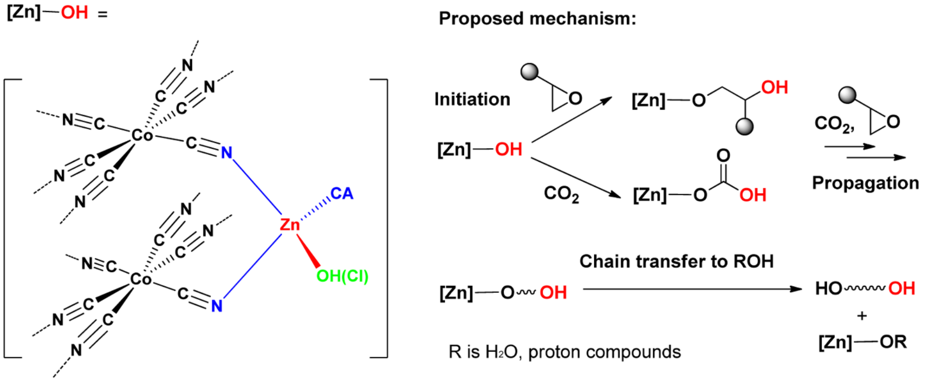


Figure 1. Possible ground-state structure of the active site of Zn−Co(III) DMCC catalyst (left) and mechanism for CO_2/epoxide copolymerization (right). Herein, two CN^- groups are shared by Zn^{2+} and Co^{3+} ions. They contain one negative charge in one tetrahedral Zn^{2+} structure. Thus, the structure meets the electroneutrality principle because of the existence of OH^- (and Cl^-) based on the elemental results, FT-IR spectrum and characterization of the polymer end groups.[28] CA is the complexing agent (generally H_2O and *t*-BuOH).

Nozaki et al. reported the copolymerization of 1,2-hexene oxide with CO_2 using a Co(III) complex with a piperidinium end-capping arm at 25 °C within 48 h. This afforded a copolymer with 98% polycarbonate selectivity.[11] Nevertheless, the copolymerization of CO_2 with epoxides with long linear alkyl chain is still a big challenge. Moreover, the copolymerization of CO_2 and epoxides with bulky branched alkyl groups such as isobutene oxide[12] and 2-*tert*-butyloxirane has not yet been reported. A recent attempt to copolymerize of isobutene oxide with CO_2 via a (Salen)Cr(III) complex with PPN azide as the catalyst promoter led to an exclusive cyclic carbonate.[12] The copolymers from CO_2 and the epoxides with branched alkyl groups produce copolymers with high T_gs, and thus this is also an attractive topic in the field.

On the other hand, the copolymerization of CO_2 with epoxides with anchoring aryl groups is equally rare,[13−17] although the resulting copolymers from CO_2 and these epoxides had a relatively high T_gs and strong intermolecular interactions that could improve the mechanical properties of the materials. Lu and Daresnbourget al.[13] reported a perfect alternating CO_2/styrene oxide (SO) copolymerization using a (Salen)Co(III) complex anchoring 1,5,7-triabiabicyclo[4,4,0]dec-5-ene and (Salen)Cr(III)/(PPN)Cl at 25 °C, which afforded a fully alternating poly(styrene carbonate) (PSC). Recently, our group reported an alternating and regioregular PSC with an alternating degree of 99.4% and 96% head-to-tail (HT) connectivity using nanosized zinc−cobalt(III) double metal cyanide complex [Zn−Co(III)DMCC] catalysts without introducing any cocatalysts or catalyst promoters.[14] Such PSC presented a T_g of 82 °C, which was higher than that of CO_2/PO copolymer (ca. 35−42 °C) and could be used as a plastic with good thermal properties.

Thus, far, a considerable number of catalyst systems[2,3,5,6,18] have been developed to synthesize CO_2/epoxide copolymers, but few of these can catalyze the copolymerization of CO_2 with many kinds of epoxides with different substituents. This is likely due to limitations in structural matching of the catalysts and epoxides with respect to their steric/electronic effects. To date, two kinds of catalyst systems could catalyze the copolymerization of CO_2 with many kinds of epoxides with good efficiency. One is the (Salen)M(III) (M = Co, Cr) complex/catalyst promoter systems[6] including both bifunctional[19−21] and two component[22−26] systems. These are highly active due to the perfectly alternating copolymerization of CO_2 with many epoxides. The CO_2/epoxide copolymerization could be precisely tuned by subtle design of the organic backbone of the catalyst. However, these syntheses are complex with multistep operations. In most cases, low temperature polymerizations are required to avoid cyclic carbonate generation.

The other catalyst is nanosized Zn−Co(III) DMCC,[27] which is a highly efficient catalyst for CO_2/epoxide copolymerization without any cocatalyst or catalyst promoters.[14,16,28,29] Recently, a nanolamellar Zn−Co(III) DMCC was observed to effectively catalyze the alternating copolymerization of CO_2 with epoxides with long side alkyl groups.[30] These results led us to systematically study the substituent effects of the epoxides on the alternating copolymerization of CO_2/epoxide using this catalyst. We obtained CO_2/epoxide copolymers with various T_gs across a wide range of temperatures. A regioselective CO_2/epoxide copolymerization style induced by bulky and electron-donating substituents via Zn−Co(III) DMCC catalysis was also proposed.

■ RESULTS AND DISCUSSION

Brief Introduction of Zn−Co(III) DMCC Catalyst. Zn−Co(III) DMCC was early discovered to be an efficient catalyst for ring-opening polymerization of epoxides, especially PO.[31,32] It is still industrially used to produce poly(propylene oxide) polyols with moderate and high molecular weights, which are widely used for making soft polyurethanes. In 1985, Kruper et al. applied Zn−Co(III) DMCC to CO_2/epoxide copolymerization for the first time.[33] Many research groups subsequently studied its preparation and application for synthesizing CO_2-based copolymers.[34−38] The traditional preparation of Zn−Co(III) DMCC involves room temperature schemes via a precipitation reaction with excess $ZnCl_2$ and $K_3Co(CN)_6$ in water/*tert*-butanol (*t*-BuOH) solution.[39] The resulting catalyst presents irregular lumps with several to dozens of micrometers and showed moderate productivity and low polycarbonate selectivity toward CO_2/epoxide copolymerization. The empirical formula of this catalyst is $Zn_3[Co(CN)_6]_2{\cdot}xZnCl_2{\cdot}y\mathrm{CA}{\cdot}zH_2O$ (CA is the complexing agent). It is nonstoichiometric because *x, y*, and *z* varied with the methods and batches of the preparation. The basic bulk structure of this catalyst shows that the cyanide bridges link zinc and cobalt atoms, but the catalytic center has not yet been disclosed. Changes in either the cobalt ion or zinc ion, e.g., $Zn[Ni(CN)_4]$[40] and $Co[Ni(CN)_4]$,[41] and substitution of one of the cyanide ions results in a dramatic change in the catalytic activity and polycarbonate selectivity.[40] The Zn−Co(III)

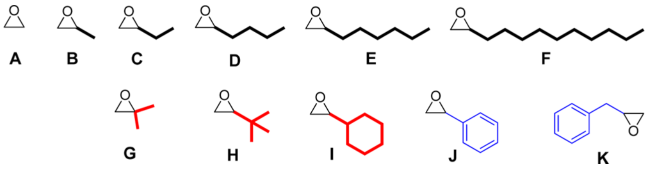
DMCC prepared using *t*-BuOH as a CA remains the best for epoxide-involved polymerizations.[42]

We proposed a hydrothermal method to synthesize Zn−Co(III) DMCC for highly active and selective CO_2/epoxide copolymerization.[27] The resulting catalyst was thermally stable, air and moisture insensitive and had unique nanolamellar and nanoporous structures with high a BET surface area of >500 m^2/g. Such nanosized structure could accommodate more catalytic sites on the surface of the catalyst and thus improved the catalytic activity toward CO_2/epoxide copolymerization.[27]

The Zn/Co molar ratio of the initial Zn−Co(III) DMCC varied depending on the preparation conditions, while the Zn/Co molar ratio of the nanosized Zn−Co(III) DMCC via hydrothermal process was ca. 2.0 and was constant across different conditions.[14,27,29] Therefore, the molar ratio of Zn^{2+}:Co^{3+}:CN^- was 2:1:6 based on the perfect coordination reaction of Zn^{2+} with $Co(CN)_6^{3-}$ via $K_3Co(CN)_6$. The $Zn_2[Co(CN)_6](OH)_aCl_b \cdot yCA\cdot z H_2O$ ($a + b = 1$) structure of Zn−Co(III) DMCC meets the electroneutrality principle because Cl^- was observed by elemental analysis and OH^- was confirmed by FT-IR spectrum (samples with CA and water removed by heat).[28] The catalytic center of this species was a zinc−hydroxyl bond (Zn−OH) based on the fact that the resulting polymers had two terminal −OH groups. In structure, the Zn−OH bond could be regarded as a Lewis acid (Zn^{2+})-base (OH^-) center, which could activate the epoxide and CO_2 collaboratively.[28] The proposed mechanism for the chain initiation, propagation and transfer reaction for Zn−Co(III) DMCC-catalyzed CO_2/epoxide copolymerization is shown in Figure 1.[28] Note that the complexes, $Zn_2[Co(CN)_6]OH$[43] and $Zn_2[Co(CN)_6]Cl$ had no any catalytic activity toward CO_2/epoxide copolymerization. This demonstrates that the activity of this catalyst might be originated from $Zn_2[Co(CN)_6](OH)_aCl_b$, although its real structure still needs ongoing investigation. Herein, we present our continued investigation concerning the CO_2/epoxide copolymerization via nanosized Zn−Co(III) DMCC catalysts for improved understanding of the substituent effects of epoxides.

Copolymerization of CO_2 with Selected Epoxides. Eleven epoxides (Scheme 1) with various substituents were successfully copolymerized with CO_2 using nanosized Zn−Co(III) DMCC. Thereof, the copolymerization of CO_2 with epoxides **A**, **C**−**E** and **G**−**I** were reported for the first time with our Zn−Co(III) DMCC catalyst. Species **B**, **C**, **D**, **E** and **F** were the epoxides with pendant linear alkyl groups with carbon numbers of 1, 2, 4, 6 and 10, respectively. **J** and **K** were epoxides with the pendant electron-withdrawing aryl groups.[14] **G**, **H**, and **I** were the epoxides with branched alkyl groups with carbon numbers of 2, 4 and 6, respectively.

Scheme 1. Selected Epoxides with Alkyl and Aryl Groups for the Copolymerization with CO_2 with Nanosized Zn−Co(III) DMCC Catalysts[a]



[a]Key: **A**, ethylene oxide, **B**, propylene oxide, **C**, 2-ethyloxirane (1,2-butene oxide), **D**, 2-butyloxirane (1,2-hexene oxide), **E**, 2-hexyloxirane (1,2-octene oxide), **F**, 2-decyloxirane (1,2-epoxydodecane), **G**, isobutene oxide, **H**, 2-(*tert*-butyl)oxirane, **I**, 2-cyclohexyloxirane, **J**, styrene oxide; **K**, 2-benzyloxirane. The syntheses of **I** and **K** are given in the Supporting Information part (see Figures S1 and S2).

The copolymerization data for the above-mentioned epoxides and CO_2 catalyzed by Zn−Co(III) DMCC are summarized in Table 1. The minimum reaction temperature was 50 °C for activating the copolymerization of CO_2 with most of the selected epoxides. However, the minimum temperature for activating the copolymerization of the epoxides **H**, **I**, and **K** with CO_2 within 15 h was 60 °C (Table 1, entries 8−9 and 11). Moreover, relatively more amounts of the catalyst (10.0 mg for 3.0 mL epoxide) was loaded for each polymerization to ensure activation of all the epoxides.

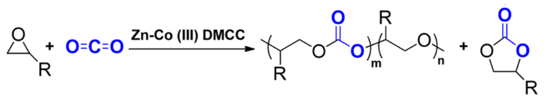
In a typical polymerization process, 3.0 mL epoxide was nearly completely converted to products (including the cyclic carbonate) with 10.0 mg Zn−Co(III) DMCC at 50 °C and 4.0 MPa CO_2 pressure within 15 h as indicated by the ^1H NMR spectra of the crude products (Figures S3−S5). This indicated the highly effective catalytic activity of Zn−Co(III) DMCC for these CO_2/epoxide copolymerizations. The productivities for CO_2 with epoxides **C**, **D**, **E**, and **F** were 1328, 1070, 1120, and 1184 g polymer/g Zn, respectively—values closer to that of CO_2/**B** (i.e., PO) copolymerization. A previously reported Zn−Co(III) DMCC catalyst prepared with poly(tetramethylene ether glycol) as a complexing agent presented no activity to CO_2/**D** copolymerization at 50 °C within 24 h.[44] Clearly, nanosized Zn−Co(III) DMCC presented higher catalytic ability toward the copolymerization of CO_2 with epoxides containing long linear alkyl groups than those with reported analogues.

The productivities of CO_2/**G** and CO_2/**H** copolymers were lower than that of CO_2/**B** copolymer because of the production of relatively more amounts of cyclic carbonate (entries 7 and 8 in Table 1). Moreover, the productivity of CO_2/**J** copolymer was 752 g of polymer/g of Zn—much less than that of CO_2/**B** copolymer because of the low reactivity of **J** under Zn−Co(III) DMCC catalysis.[14] Long linear alkyl groups could lead to a CO_2/epoxide copolymer with high number-average molecular weight (M_n) because the long linear alkyl group could suppress the chain transfer reaction to trace water in the system along as well as backbiting reactions that decrease M_n. We found that the branched alkyl groups and aryl groups of the epoxides also resulted in CO_2/epoxide copolymers with relatively low M_ns (Table 1) and relatively more amounts of cyclic carbonates.

The alternating degree (F_{CO_2}) of the resulting CO_2/epoxide copolymers and the weight percentage of the cyclic carbonate in the total products (W_{CC}) were then used to evaluate the polycarbonate selectivity of the catalyst. Moreover, the selective ring-opening reaction of the epoxide produced a regioregular copolymer. Such regioselectivity could be evaluated by the content of the head-to-tail (HT) connectivity of the resulting copolymer based on the ^{13}C NMR spectrum.[45] Herein, the substituent effects of the epoxides on CO_2/epoxide copolymerization were illustrated with the above parameters.

Alternating Degree (F_{CO_2}). The increase in the length of the pendant linear alkyl group of the epoxide led to a high F_{CO_2} of the resulting copolymers. As shown in Figure 2, the longer the pendent alkyl groups, the higher F_{CO_2} was achieved. Ethylene oxide (**A**)/CO_2 copolymer showed an F_{CO_2} of 55.3% (entry 1 in Table 1, spectrum 1 in Figure 2). For the copolymer of CO_2/**B** with a side methyl group, the F_{CO_2} increased to 73.2% under the same experimental conditions (entry 2 in Table 1). The F_{CO_2}

Table 1. Copolymerization of CO_2 with Various Mono-Substituted Epoxides Using Zn–Co(III) DMCC Catalyst (R Represents the Substituent of the Epoxide)[a]



entry	epoxides	temp (°C)	F_{CO_2} (%)[b]	W_{CC} (wt %)[b]	M_n (kg/mol)[c]	PDI[c]	productivity[d] (g polymer/g Zn)	convn (%)[e]	T_g (°C)
1	**A**	50	55.3	14.2	0.9	2.3	925	98	−1
2	**B**	50	73.2	5.7	21.2	2.4	1215	88	14
3	**C**	50	91.5	4.8	24.6	4.6	1328	100	6
4	**D**	50	95.6	2.7	19.2	5.0	1070	100	−18
5	**E**	50	98.6	2.0	48.7	4.0	1120	100	−27
6	**F**	50	>99.0	1.1	93.2	4.5	1184	100	−38
7	**G**	50	>99.0	20.0	6.6	2.0	993	100	35
8	**H**	60	>99.0	13.0	44.6	2.5	750	86.5	53
9	**I**	60	>99.0	1.5	20.0	2.9	1210	100	84
10	**J**	50	94.2	3.0	12.7	3.0	752	80.6	76
11	**K**	60	99.0	1.8	16.1	3.9	1094	100	78

[a] Reaction conditions: Zn–Co(III) DMCC, 10.0 mg; epoxide, 3.0 mL; CO_2, 4.0 MPa; 50 °C; 15 h. [b] Calculated from ^{1}H NMR spectroscopy, $F_{CO_2} = (A_{\text{carbonate linkage}})/[(A_{\text{carbonate linkage}} + A_{\text{ether linkage}}), W_{cc} = A_{\text{cyclic carbonate}}M_{\text{cyclic carbonate}}/[M_{\text{cyclic carbonate}}(A_{\text{cyclic carbonate}} + A_{\text{carbonate linkage}}) + M_{\text{ether unit}}A_{\text{ether linakes}}]$. Term A represents the integral area, and M represents the molecular weight. [c] Determined by gel permeation chromatography (GPC) calibrated with monodisperse polystyrene standards in THF at 40 °C. [d] The productivity was defined as g polymer/g Zn. [e] Including the copolymer and cyclic carbonates, EO conversion from ^{1}H NMR determination might be on the high side due to its low boiling point of 10.4 °C.

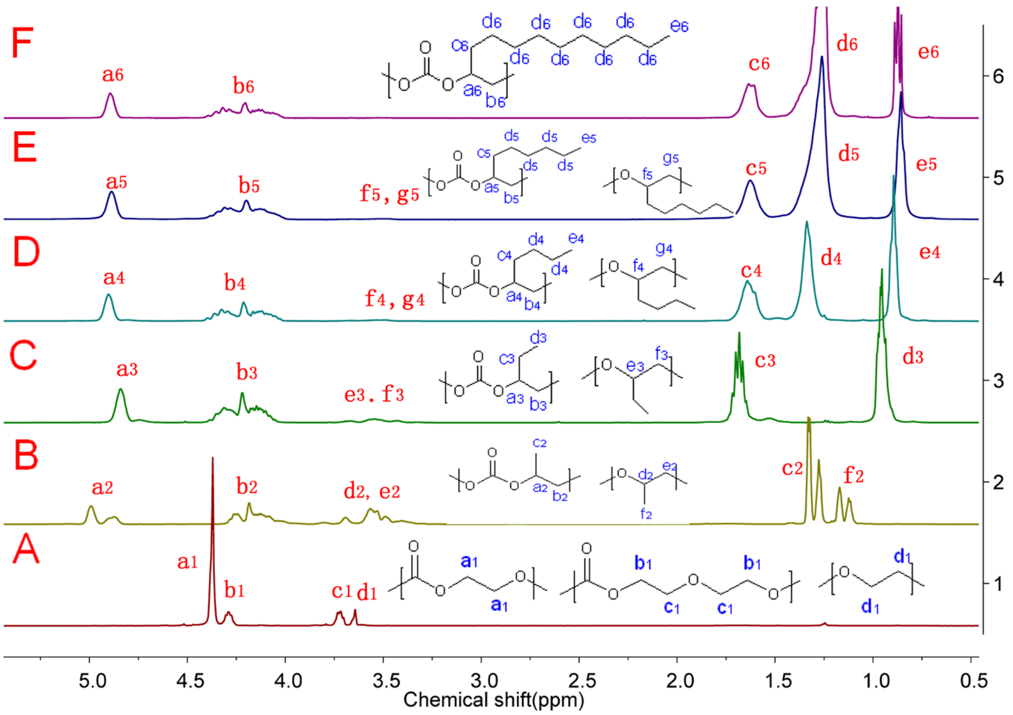


Figure 2. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the purified CO_2/epoxide copolymers from **A-E** via Zn–Co(III) DMCC catalysis at 50 °C, 4.0 MPa CO_2 pressure and 15 h.

values of CO_2/**C**, CO_2/**D**, CO_2/**E** and CO_2/**F** copolymers were 91.5%, 95.6%, 98.6%, and >99%, respectively (entries 3–6 in Table 1). They increased with increasing number of carbons on the pendant alkyl group. This result could be explained by intramolecular steric repulsion effects through the formation of two neighboring CO_2/epoxide carbonate units. When the CO_2 copolymerized with epoxides containing long alkyl groups, the resulting polymer chain had a "crowded" side alkyl group,[30,46] and thus it increased the steric hindrance, which hampered the continuous epoxide insertion.[46]

When the number of carbons on the epoxide pendant groups was the same, the branched pendant groups led to a clear improvement in F_{CO_2}. The CO_2/**H** copolymer has a F_{CO_2} of >99% (**H** in Figure 3), which was higher than that of CO_2/**D** copolymer, i.e. 95.6% (**D** in Figure 2). Similar data was observed when comparing F_{CO_2} of CO_2/**E** copolymer (98.6%) with that of CO_2/**I** copolymer (>99%). Clearly, both **H** and **I** with branched alkyl groups presented more significant steric repulsion effects than **D** and **E** with linear alkyl groups. Species **G** with two substituted methyls provided strong steric hindrance on the

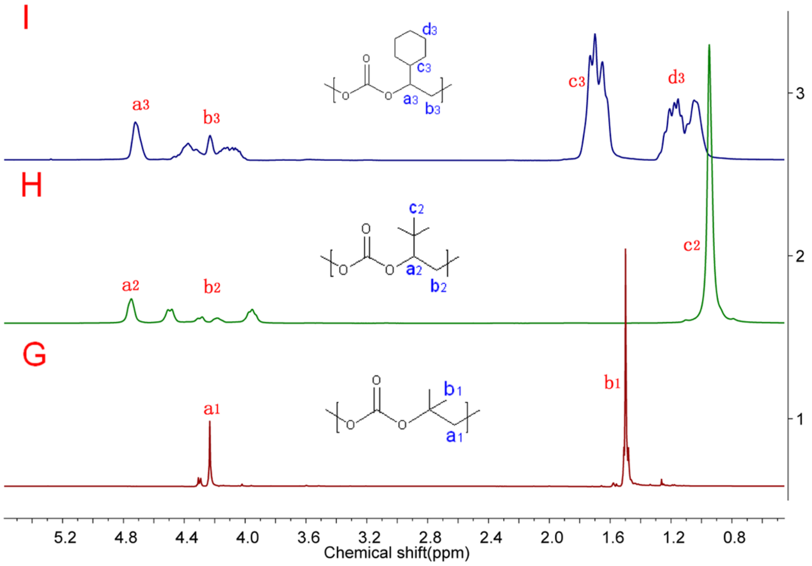


Figure 3. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the purified copolymers from **G, H** and **I** via Zn−Co(III) DMCC catalysis at 60 °C (for **G**, 50 °C), 4.0 MPa CO_2 pressure and 15 h.

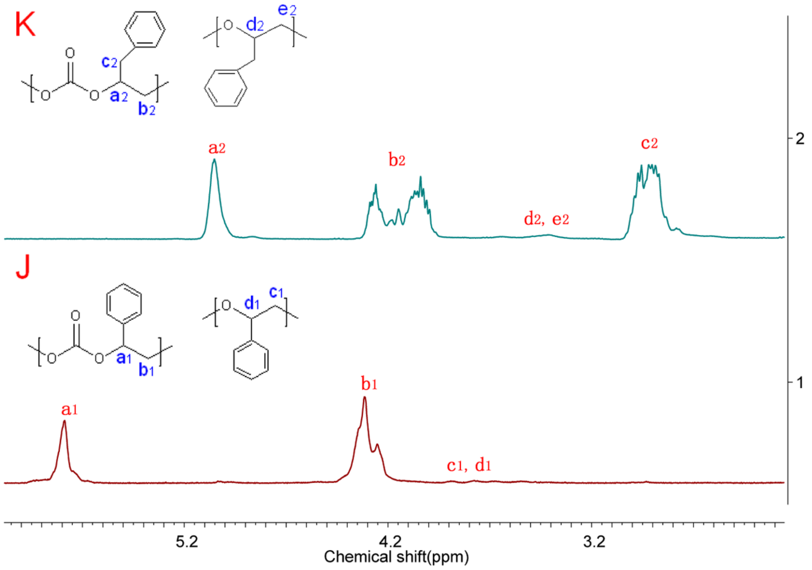


Figure 4. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the purified copolymers from CO_2 with epoxides **J** and **K** with side electron-withdrawing groups.

copolymerization and led to the production of a CO_2/**G** copolymer with an F_{CO_2} of >99% (**G** in Figure 3). This was higher than that of the CO_2/**C** copolymer with a side ethyl group (91.5%).

The steric hindrance of the electron-withdrawing substituents of the epoxides also favored to improve of the alternating degrees of the resulting copolymers. As shown in Figure 4, the F_{CO_2} of the resulting copolymers from the copolymerization of CO_2 with epoxides **J** and **K** followed the sequence order of the steric hindrance of **J** (94.2%, 50 °C) < **K** (99.0%, 60 °C), which was consistent with our previous report at different reaction temperatures.[14]

The above results indicated that Zn−Co(III) DMCC was an effective catalyst for the copolymerization of CO_2 with various epoxides containing long pendent linear and branched alkyl groups. It afforded alternating CO_2/epoxide copolymers. The alternating degree of the CO_2/epoxide copolymer via Zn−Co(III) DMCC catalysis was determined by the steric hindrance of the pendant groups of the monosubstituted epoxides regardless of whether such pendant groups had electron-donating or withdrawing properties.

Production of Cyclic Carbonate (W_{CC}). The formation of the cyclic carbonate during CO_2/epoxide copolymerization mainly resulted from the backbiting reaction of the end carbonate anions.[47] Therefore, the production of cyclic carbonate was closely correlated to the properties of the pendent group of the epoxides under Zn−Co(III) DMCC catalysis.

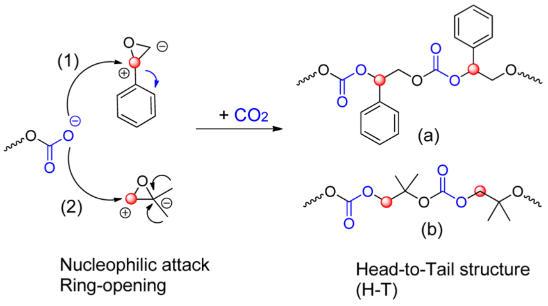
For the epoxides with linear alkyl groups shown in Table 1 (Figure S3, ^{1}H NMR spectra of the crude products), the content of the cyclic carbonate W_{CC} decreased from 14.2 to 1.1 wt % with increasing carbon numbers from 0 to 10 for epoxides **A**, **B**, **C**, **D**, **E**, and **F** (entries 1−6, Table 1). That is, increasing the length of the pendant alkyl group inhibited the production of cyclic carbonates. This result could be attributed to the intramolecular steric repulsion effects of the long side alkyl group of the copolymer,[30,46] which hampered the backbiting reaction.

Surprisingly, the copolymerization of epoxides **G** and **H** with CO_2 resulted in the production of considerable amounts of cyclic carbonates of 20 and 13 wt % (Figure S4, ^1H NMR spectra of the crude products), respectively. These values were clearly higher than those achieved with epoxides **C** and **D** that contain side groups with the same number of carbons. This result indicated that the stronger steric hindrance and electron-donating ability of the dimethyl and tertiary butyl groups favored the backbiting reaction and formed cyclic carbonate.

Interestingly, for epoxides **I** and **J** in which cyclohexyl and phenyl had the same carbon numbers, the CO_2/**J** copolymerization gave relatively higher amounts of the cyclic carbonate in the product (4.9 wt %), which indicates that the substituents with more electron-withdrawing groups favored the production of the cyclic carbonate. The copolymerization of CO_2 with **K**, which has a less electron-withdrawing benzyl group, also gave a lower W_{CC} (1.8 wt %, 60 °C) than that of CO_2/**J** copolymer (4.9 wt %, 60 °C, Figure S5) containing a phenyl group. These results indicated that Zn−Co(III) DMCC was excellent for the CO_2/epoxide copolymerization because relatively small amounts of cyclic carbonates were produced at 50−60 °C for the most of epoxides in Table 1. In contrast, most of the reported catalysts required low reaction temperatures to avoid production of cyclic carbonates.

Regioselectivity. It is of great interest to investigate the regiochemistry of the CO_2/epoxide copolymerization because regioregular CO_2/epoxide copolymers should expand the range of the thermal and mechanical properties of the resulting copolymers versus their regioirregular counterparts.[10,13,15,45,48] Here, CO_2/epoxide copolymers with highly alternating degrees (94.2% - >99%, entries 4−11 in Table 1) were selected for further analysis of regiochemistry because the carbonate anion ($-OOCO^-$) was the main nucleophilic species attacking the methylene (CH_2) or methine (CH) sites to open the epoxide ring (Scheme 2).

Scheme 2. Proposed Mechanism for Regioselective CO_2/J and CO_2/G Copolymerization via Zn−Co (III) DMCC Catalysis[a]



[a]The red dot in the backbone represents the site proposed for attack by the carbonate anion.

CO_2/**J** copolymerization was highly regioselective under Zn−Co(III) DMCC catalysis[14] and afforded a CO_2/**J** copolymer with 90% HT connectivity (50 °C). In this instance, the electron-withdrawing phenyl group made the CH site more positive than the CH_2 site, and thus the carbonate anion predominantly attacked the CH site of **J** (route 1 in Scheme 2) although the CH site had significant steric hindrance due to the phenyl group. This result highlights that the counteracting effect of steric hindrance on regioselectivity could be minimized. When the phenyl group was substituted by a benzyl group (**K**) with less electron-withdrawing ability, the resulting CO_2/**K** copolymer only had a 77% HT connectivity (60 °C).

Because the electron-withdrawing phenyl group of **J** predominantly induced nucleophilic attack on the carbonate anion to CH site, we wondered whether the strong electron-donating ability and steric hindrance of the branched alkyl group linked to the epoxide (**G**, **H** and **I**) would lead a ring-opening event at the less substituted CH_2 site (e.g., route 2 in Scheme 2). Indeed, the CH_2 sites of **G**, **H** and **I** had more positive charges than the substituted carbon, and thus favored nucleophilic attack of the carbonate anion.

The epoxide **G** is special in structure because it has two substituted methyls at the quaternary carbon making it achiral. Therefore, the microstructure of the resulting poly(isobutene carbonate) would be simpler than those with chiral carbons. The ^{13}C NMR spectrum of poly(isobutene carbonate) in the carbonyl region exhibits one sharp peak at δ_C 153.0 ppm and two small peaks at δ_C 154.9 and 151.3 ppm (Figure 5). The three peaks at δ_C 154.9, 153.0, and 151.3 ppm could be ascribed to HH, HT and TT connectivity of the poly(isobutene carbonate), respectively. The proposed HH, HT and TT connectivity of poly(isobutene carbonate) could also be qualified by a random copolymer model using ethylene oxide (EO), cyclohexene oxide (CHO) and CO_2. In this model, the three carbonyl regions of EO−CO_2-EO (154.9 ppm), EO-$\underline{C}O_2$−CHO (154.2 ppm) and CHO−CO_2−CHO (153.2−153.7 ppm) caused by random terpolyemrization were similar to the chemical environments with TT, HT and HH connectivity of the poly(isobutene carbonate), respectively.[49,50]

Moreover, the ^{13}C NMR spectrum for the other quaternary carbons of poly(isobutene carbonate) only showed a single sharp peak at δ_C 81.5 ppm (Figure 5), which is also indicative of the oversimplified chemical environment around this quaternary carbon. Therefore, poly(isobutene oxide) is proposed to be a regioregular copolymer with high HT connectivity, which was calculated to be 83% based on the integral area ratio of these peaks. The strong and direct electron-donating ability of the two methyls toward the quaternary carbon of **G** induced the carbonate anion to attack the CH_2 site with a more positive charge (Scheme 2). Moreover, the steric hindrance of the two methyls could hinder and repel attack of the carbonate anion to the quaternary carbon of **G**.

The CO_2/**H** copolymer with a side tertiary butyl group was also expected to have a regioregular structure to some extent because the tertiary butyl group has strong electron-donating ability and steric hindrance. However, it was difficult to determine the regioregular structure of CO_2/**H** copolymer based only on the peak splitting data for the carbonyl region in the ^{13}C NMR spectrum (Figure S7). We did observe two asymmetric neighboring peaks at δ_C 155.0 ppm. Because **H** has a chiral CH site, we attempted to probe the regioregular structure of the CO_2/**H** copolymer by determining the optical properties of the hydrolyzed CO_2/(*S*)-**H** copolymer via Zn−Co(III) DMCC from an optically active epoxide (*S*)-**H**. This was because the (*S*)-configuration of the carbonate unit of the CO_2/(*S*)-**H** copolymer would be retained after hydrolysis if the (*S*)-**H** copolymerized with CO_2 through a regioselective attack on the CH_2 site of (*S*)-**H**. However, we failed to resolve the racemic mixture of **H** needed to obtain pure (*S*)-**H** via an (*R*)-(Salen)Co complex (see Supporting Information part). Indeed, the bulky tertiary butyl group of **H** hampered the resolution.[51] Similarly, the microstructure of the CO_2/**I** copolymer (Figure S8) was also difficult to determine.

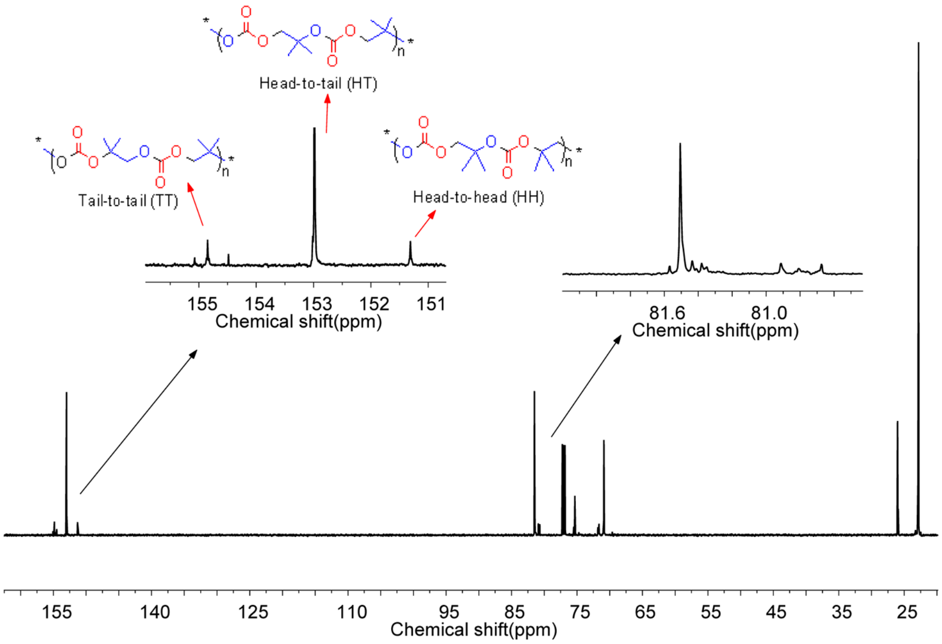


Figure 5. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of poly(isobutene oxide) from CO_2/**G** copolymerization with Zn−Co(III) DMCC. Key: TT = tail-to-tail; HT = head-to-head; HH = head-to-head.

In contrast to the regioregular CO_2/**J** copolymer, the CO_2/**G** copolymer presented a relatively low content for the HT connectivity (90% vs 83%) suggesting that the ability of the bulky electron-donating alkyl groups to induce a regioselective ring-opening reaction at the CH (or C) site of the epoxide was weaker than that of the aryl group for a regioselective ring-opening reaction at the CH_2 site. This was further proved by the fact that the copolymerization of CO_2 and **B**—with one methyl group and thus less electron-donating behavior—leads to a complete regioirregular copolymer. Even increasing the length of the pendant linear alkyl groups (i.e., keeping the electron-donating ability but enhancing the steric hindrance) gave no regioselective copolymerization. The ^{13}C NMR spectra of the CO_2/**D**, CO_2/**E**, and CO_2/**F** copolymers in the carbonate region show several overlapping peaks, which were similar to that of the CO_2/**B** copolymers (Figure S6). The contents of HT connectivity of these copolymers were roughly estimated to be 52%. This implied no stereoselectivity in the epoxide ring-opening step.

As discussed above, the regioselective CO_2/epoxide copolymerization via Zn−Co(III) DMCC catalysis was mainly determined by the electron induction effect of the epoxide rather than the steric hindrance of the substituents. Indeed, it is a meaningful topic in the field of CO_2 copolymerization that the regioselective ring-opening reaction happens at CH_2 site of the epoxides with alkyl group (e.g., **B**) during copolymerization with CO_2. The Lu group has reported an elegant work on regioselective CO_2/**B** copolymerization through subtle design of bifunctional (Salen)Co(III) complexes.[10] In the present work, Zn−Co(III) DMCC is active for many epoxides to copolymerize with CO_2, which provides a chance to look into the substituent effects of the epoxide on the regioselectivity of the CO_2/epoxide copolymerization.

Glass Transition Temperatures (T_gs). The epoxide substituents had a strong impact on the T_gs of the CO_2/epoxide copolymers (Figure 6). The T_gs of the copolymers ranged from −38 to +84 °C, depending on the substituent groups of the epoxide. The T_gs of the copolymers with side linear groups decreased from +6 to −38 °C with increasing lengths of the side chain from C2 to C10 because the longer side linear alkyl group caused stronger plasticizing effects and regioirregular microstructures. Herein, the T_g of the CO_2/**C** copolymer was 6 °C, which was lower than that of fully alternating CO_2/**C** copolymer (i.e., 9 °C).[12] Importantly, it is also possible to regulate T_g of the CO_2/epoxide copolymer via Zn−Co(III) DMCC catalysis by tuning the reaction temperature and CO_2 pressure.[29,52]

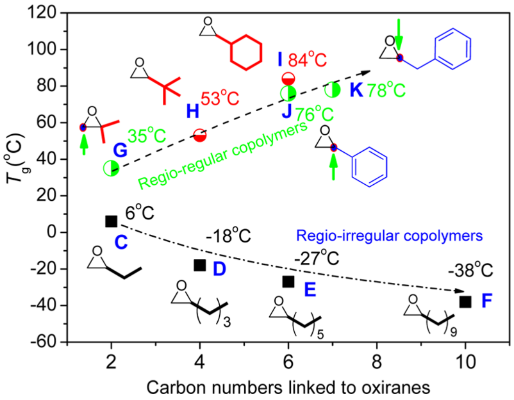


Figure 6. Substituent effect of the epoxides on the glass transition temperatures (T_gs) of the resulting CO_2/epoxide copolymers (F_{CO_2} = 91.5−99%; M_n = 6.6−93.2 kg/mol).

For copolymers with side branched alkyl and aryl groups, the T_gs increased from 35 to 84 °C with increasing steric hindrance (i.e., carbon numbers C2, C4, and C6 to C7) of the substituent groups. This could effectively inhibit the free rotation of the backbone. Moreover, the CO_2/**K** and CO_2/**J** copolymers with regioregular microstructures improved the T_gs.[14] The copolymers with branched side groups had higher T_gs than their linear counterparts. This is seen when comparing the CO_2/**C** copolymer (6 °C) with CO_2/**G** copolymer (35 °C), CO_2/**D** copolymer (−18 °C) with CO_2/**H** copolymer (53 °C) and CO_2/**E** copolymer (−27 °C) with CO_2/**I** (84 °C) copolymer.

Therefore, various CO_2/epoxide copolymers with wide T_g ranges from −38 to 84 °C could be obtained with the Zn−Co(III) DMCC catalyst. These could potentially be used as elastomers or plastics.[29,52,53]

CONCLUSIONS

The substituent effect of the epoxides on CO_2/epoxide copolymerization with nanosized Zn−Co(III) DMCC was systematically investigated. The F_{CO_2} of the resulting CO_2/epoxide copolymers was determined by the steric effect of the substituents of the epoxides, while the regioselective CO_2/epoxide copolymerization was dominated by the electron induction effect of the substituents. The electron-withdrawing group could effectively induce the regioselective copolymerization. A new regioselective reaction at the CH_2 site of CO_2/isobutene oxide copolymerization was observed and attributed to the strong electron-donating ability of the two methyls of isobutene oxide. The correlation of T_g with the substituents of the CO_2/epoxide copolymers was discussed. Various CO_2/epoxide copolymers with a wide range of the T_g values (−38 to +84 °C) were obtained.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving general experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci, Part C: Polym. Lett.* **1969**, *7*, 287−292.

(2) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(3) Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Ed* **2004**, *43*, 6618−6639.

(4) Sugimoto, H.; Inoue, S. *J. Polym. Sci, Part A: Polym. Chem.* **2004**, *42*, 5561−5573.

(5) Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 141−163.

(6) (a) Lu, X. B.; Ren, W. M.; Wu, G. P. *Acc. Chem. Res.* **2012**, *45*, 1721−1735. (b) Lu, X. B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462−1484.

(7) Lee, B. Y.; Cyriac, A. *Nat. Chem.* **2011**, *3*, 505−507.

(8) For production and application of CO_2-based copolymer, see Web sites: (a) . Novomer: Carbon Dioxide, http://www.novomer.com/?action=CO2;. (b) . Bangfeng Technology: http://www.cn-bf.net/en/;. (c) . ZhongkeJinLong: http://www.zhongkejinlong.com.cn/en/index.asp;. (d) . Nanyang Zhongju Tianguan Low Carbon Technology: http://www.tgnbm.com/cpzx/111.htm;. (e) . Empower Materials: www.empowermaterials.com. (f) . Aschenbrenner, N.; Kunze, K. *Green Polymer Made of CO_2 from Exhaust Gases*, http://www.siemens.com/innovation/en/news/2012/e_inno_1213_2.htm;. (h) . Econic Technologies: Polymers from CO_2, http://www.econic-technologies.com/.

(9) Allen, S. D.; Byrne, C. M.; Coates, G. W. Feedstocks for the Future: Renewables for the Production of Chemicals and Materials. *ACS Symp. Ser.* **2006**, *921*, 116−128.

(10) Lu, X. B.; Shi, L.; Wang, Y. M.; Zhang, R.; Zhang, Y. J.; Peng, X. J.; Zhang, Z. C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664−1674.

(11) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem. Int. Ed* **2006**, *118*, 7432−7435.

(12) Darensbourg, D. J.; Chung, W.-C. *Macromolecules* **2014**, *47*, 4943−4948.

(13) Wu, G. P.; Wei, S. H.; Lu, X. B.; Ren, W. M.; Darensbourg, D. J. *Macromolecules* **2010**, *43*, 9202−9204.

(14) Wei, R. J.; Zhang, X. H.; Du, B. Y.; Sun, X. K.; Fan, Z. Q.; Qi, G. R. *Macromolecules* **2013**, *46*, 3693−3697.

(15) Wu, G. P.; Wei, S. H.; Ren, W. M.; Lu, X. B.; Xu, T. Q.; Darensbourg, D. J. *J. Am. Chem. Soc.* **2011**, *133*, 15191−15199.

(16) Wei, R. J.; Zhang, X. H.; Du, B. Y.; Fan, Z. Q.; Qi, G. R. *Polymer* **2013**, *54*, 6357−6362.

(17) Hu, Y.; Qiao, L.; Qin, Y.; Zhao, X.; Chen, X.; Wang, X.; Wang, F. *Macromolecules* **2009**, *42*, 9251−9254.

(18) Luinstra, G. A.; Haas, G. R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. *Chem.—Eur. J.* **2005**, *11*, 6298−6314.

(19) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem. Int. Ed* **2006**, *45*, 7274−7277.

(20) Noh, E. K.; Na, S. J.; S, S.; Kim, S. W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082−8083.

(21) Ren, W. M.; Liu, Z. W.; Wen, Y. Q.; Zhang, R.; Lu, X.-B. *J. Am. Chem. Soc.* **2009**, *131*, 11509−11518.

(22) (a) Lu, X.-B.; Wang, Y. *Angew. Chem. Int. Ed* **2004**, *43*, 3574−3577. (b) Zhang, J. F.; Ren, W. M.; Sun, X. K.; Meng, Y.; Du, B. Y.; Zhang, X. H. *Macromolecules* **2011**, *44*, 9882−9886.

(23) Darensbourg, D. J.; Moncada, A. I. *Macromolecules* **2009**, *42*, 4063−4070.

(24) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869−10878.

(25) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans* **2006**, 237−249.

(26) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251−6253.

(27) Sun, X. K.; Zhang, X. H.; Liu, F.; Chen, S.; Du, B. Y.; Wang, Q.; Fan, Z. Q.; Qi, G. R. *J. Polym. Sci, Part A: Polym. Chem.* **2008**, *46*, 3128−3139.

(28) Sun, X. K.; Zhang, X. H.; Wei, R. J.; Du, B. Y.; Wang, Q.; Fan, Z. Q.; Qi, G. R. *J. Polym. Sci, Part A: Polym. Chem.* **2012**, *50*, 2924−2934.

(29) Zhang, X. H.; Wei, R. J.; Sun, X. K.; Zhang, J. F.; Du, B. Y.; Fan, Z. Q.; Qi, G. R. *Polymer* **2011**, *52*, 5494−5502.

(30) (a) Zhang, Y. Y.; Zhang, X. H.; Wei, R. J.; Du, B. Y.; Fan, Z. Q.; Qi, G. R. *RSC Adv.* **2014**, *4*, 36183−36188. (b) Zhang, Y. Y.; Wei, R. J.; Zhang, X. H.; Du, B. Y.; Fan, Z. Q. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, DOI: 10.1002/pola.27497.

(31) Huang, Y. Jun.; Zhang, X. H.; Hua, Z. J. *Macromol. Chem. Phys.* **2010**, *211* (11), 1229−1237.

(32) Kim, I.; Ahn, J.-T.; Ha, C. S.; Yang, C. S.; Park, I. *Polymer* **2003**, *44*, 3417−3428.

(33) Kruper Jr, W. J.; Swart, D. J. Carbon dioxide oxirane copolymers prepared using double metal cyanide complexes. US Patent 4,500,704, 1985.

(34) Chen, S.; Hua, Z.; Fang, Z.; Qi, G. *Polymer* **2004**, *45*, 6519−6524.

(35) Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C.; Phelps, A. L. *Inorg. Chem.* **2003**, *42*, 7809−7818.

(36) Yi, M. J.; Byun, S. H.; Ha, C. S.; Park, D. W.; Kim, I. *Solid State Ionics* **2004**, *172*, 139−144.

(37) Wu, L. C.; Yu, A. F.; Zhang, M.; Liu, B. H.; Chen, L. B. *J. Appl. Polym. Sci.* **2004**, *92*, 1302−1309.

(38) Gao, Y. G.; Qin, Y. S.; Zhao, X. J.; Wang, F. S.; Wang, X. H. *J. Polym. Res.* **2012**, *19*, 1−9.

(39) Zhang, X. H.; Hua, Z. J.; Chen, S.; Liu, F.; Sun, X. K.; Qi, G. R. *Appl. Catal., A* **2007**, *325*, 91−98.

(40) Zhang, X. H.; Chen, S.; Wu, X. M.; Sun, X. K.; Liu, F.; Qi, G. R. *Chin. Chem. Lett.* **2007**, *18*, 887−890.
(41) Robertson, N. J.; Qin, Z. Q.; Dallinger, G. C.; Lobkovsky, E. B.; Lee, S.; Coates, G. W. *Dalton Trans* **2006**, 5390−5395.
(42) Sun, X. K.; Chen, S.; Zhang, X. H.; Qi, G. R. *Prog. Chem.* **2012**, *24*, 1776−1784.
(43) Kyper, J.; Boxhoorn, G. *J. Catal.* **1987**, *105*, 163−174.
(44) Kim, I.; Yi, M. J.; Byun, S. H.; Park, D. W.; Kim, B. U.; Ha, C. S. *Macromol. Symp.* **2005**, *224*, 181−192.
(45) Li, B.; Zhang, R.; Lu, X. B. *Macromolecules* **2007**, *40*, 2303−2307.
(46) Okada, A.; Kikuchi, S.; Yamada, T. *Chem. Lett.* **2011**, *40*, 209−211.
(47) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388−2410.
(48) Lu, X. B.; Ren, W. M.; Wu, G. P. *Acc. Chem. Res.* **2012**, *45*, 1721−1735.
(49) Min, J. D.; Zhang, Y. M.; Chen, Y. Y.; Wang, X. H.; Zhao, X. J.; Wang, F. S. *Acta Polym. Sin.* **2008**, *1*, 1076−1081.
(50) Zou, Y. N.; Xiao, M.; Li, X. H.; Wang, S. J.; Meng, Y. Z. *Polym. Compos.* **2007**, *15*, 53−58.
(51) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936−938.
(52) Liu, S.; Qin, Y.; Chen, X.; Wang, X.; Wang, F. *Polym. Chem.* **2014**, *5*, 6171−6179.
(53) Lim, J. W.; Oh, H. J.; Kim, Y.; Jeong, K. E.; Yim, J. H.; Ko, Y. S. *Polymer (Korea)* **2010**, *34*, 507−510.

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Regioselective and Alternating Copolymerization of Carbonyl Sulfide with Racemic Propylene Oxide

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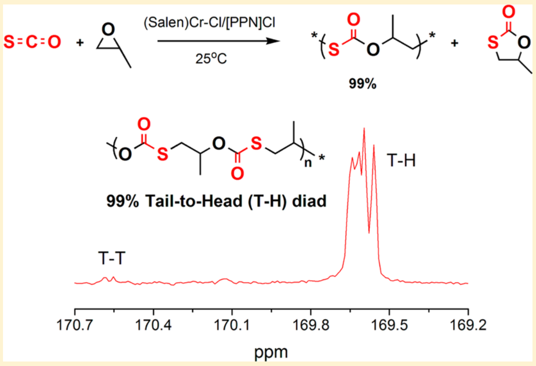
Supporting Information

ABSTRACT: We report the first example of a regioregular and fully alternating poly (propylene monothiocarbonate) (PPMTC) from the well-controlled copolymerization of two asymmetric monomers, carbonyl sulfide and racemic propylene oxide, using (Salen)CrCl in conjunction with bis(triphenylphosphoranylidene)ammonium chloride. The maximum turnover of frequency of this catalyst system was 332 h^{-1} at 25 °C. The contents of monothiocarbonate and tail-to-head linkages of PPMTC were up to 100% (based on ^{1}H NMR spectra) and 99.0% (based on ^{13}C NMR spectra), respectively. PPMTC samples have number-average molecular weight (M_n) up to 25.3 kg/mol with polydispersity index of 1.41. The very low decomposition temperature of 137 °C and high refractive index of 1.63 of PPMTC make it a potential scarifying optical adhesive.



INTRODUCTION

Carbonyl sulfide (COS) is released from the burning of fossil fuels, coal gas, many chemical processes, volcanic eruption, and plant or protein corruption. Although the COS concentration in the troposphere is currently fairly low (~500 ppt), it causes acid rain and damage of the ozonosphere by a series of photochemical reactions.[1] However, as an asymmetric organosulfur compound with heterocumulene structure, it is an resource of C═O or C═S groups for organic synthetic chemistry.[2] The fixation of COS to chemicals is an intriguing and promising topic in chemistry, but very few publications are reported to date.[3]

Because COS is structurally an analogue of CO_2 (and CS_2), we were strongly motivated to convert COS into polymers, in a way similar with the CO_2−epoxide copolymerization,[4] producing poly(thiocarbonate). This polymeric material has the potential to be applied as photoconductive fiber, heavy metal scavengers, and adhesives because of its high optical properties, excellent chemical resistance, and heavy-metal recognition ability.[5] Although polycondensation,[6] ring-opening polymerization (ROP),[7] and alternating copolymerization[3b,8] (Scheme S1 in the Supporting Information) have been utilized to synthesize poly(thiocarbonate)s, the synthesis of regioregular poly(monothiocarbonate) with asymmetric unit from direct alternating COS-epoxide copolymerization has, up until now, not been reported.

The chemistry involved in COS−epoxide copolymerization process will have all of the issues of CO_2−epoxide copolymerization, including the activity, copolymer selectivity, regioselectivity (for terminated epoxides), enantioselectivity, and control of molecular weight and polydispersity index (PDI).[4c] Moreover, two special problems will be raised when a terminated epoxide (herein propylene oxide, PO) is applied, as shown in Scheme 1.

One is that the oxygen−sulfur exchange reaction (O/S ER) between COS and PO will generate CO_2 and propylene sulfide (PS) in the system.[8b] The crossed copolymerization of the coexistent species (i.e., PO, COS, CO_2, and PS; see Table S1 in the Supporting Information) might occur and produce a copolymer with possible units as **1**−**4** (and cyclic products **1′**−**4′**) in Scheme 1, if assuming preferential coordination of the sulfur atom of COS to the active center (route **A** in Scheme 1).

The other is the stereochemistry control of COS-PO copolymerization involving the two asymmetric monomers. The coordination of the sulfur or oxygen atom of COS to the active center (route **A** or **B** in Scheme 1) will generate −SC(═O)O− and −OC(═S)O− units (**5**) and cyclic byproduct (**5′**), respectively. The occurrence of O/S ER will probably cause the generation of **6** and **6′**. Meanwhile, the attacking manner of propagating species of −OC(═O)S− via route **A** to the carbon of CH_2 or CH of PO will produce four kinds of consecutive monothiocarbonate diads: head-to-tail (H−T), tail-to-head (T−H), tail-to-tail (T−T), and head-to-head (H−H). Note that T−H diad is different from H−T diad due to asymmetric monothiocarbonate structure. All predicted units in the copolymer and cyclic (thio) carbonates are listed in Scheme 1.

Therefore, the selectivity of monothiocarbonate unit **1** depends on the depression extent of O/S ER. We hypothesized

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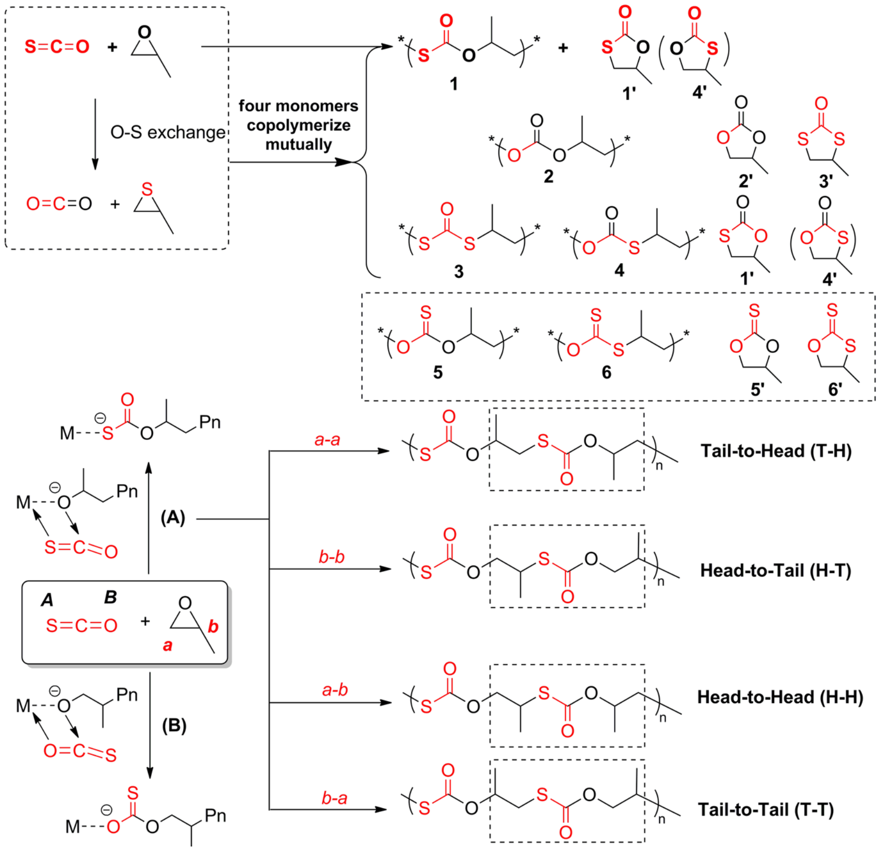
Scheme 1. Prediction of All Possible Products from COS-PO Copolymerization[a]



[a]Upper: If O−S exchange reaction occurs during copolymerization, **1**−**6** and byproducts **1′**-**6′** will be formed by the attack of propagating species to CH_2 of PO. Bottom: Four possible diads of the COS-PO copolymer formed by various regioselective attacks after route **A**.

that metal−OH could result in O/S ER because it was very active to transform CS_2 (or COS) to COS (or CO_2) in the presence of water.[9] Because metal−OH could be generated in our system via chain-transfer reaction of propagating species to trace water,[10] O/S ER could be eliminated by depressing the chain transfer reaction.

In this work, we report the synthesis of a regioregular and fully alternating poly(propylene monothiocarbonate) (PPMTC) by using (Salen)CrCl complexes as the catalysts and the confirmation of the above hypothesis. Several (Salen)CrCl complexes with various diamine backbones (**a**−**c**) were employed (Figure 1) for COS−PO copolymerization in the presence of organic bases (Figure 1, Table S2 in the Supporting Information) because they could catalyze CS_2−epoxides[8a] (and PS[8c]) copolymerization and regioselective CO_2−epoxide copolymerization.[10−12]

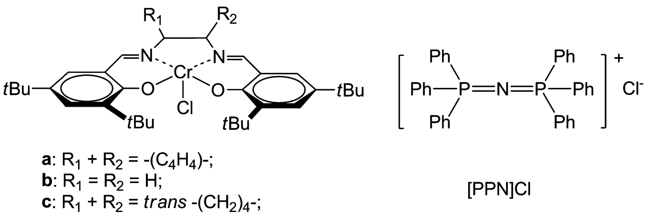
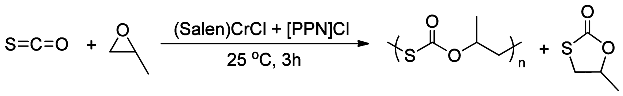


Figure 1. Binary (Salen)CrCl complex/bis(triphenylphosphoranylidene) ammonium chloride ([PPN]Cl) catalyst system used for COS-PO copolymerization.

■ EXPERIMENTAL SECTION

Method and Materials. All procedures involving air- or moisture-sensitive compounds were carried out in a glovebox under a dry argon atmosphere or with the standard Schlenk technique under dry argon. Propylene oxide (PO) was distilled under a nitrogen atmosphere after drying over CaH_2. COS (99.5%) was purchased from the Mixed Gases Company of Hangzhou New Century and used as received. All of the solvents used were distilled under a nitrogen atmosphere from CaH_2 prior to use. Most of other reagents were used without further purification unless otherwise specified. ^1H and ^{13}C NMR spectra of the resultant copolymers were performed on a Bruker Advance DMX 400 MHz spectrometer. Chemical shift values were referenced to TMS as internal standard at 0.0 ppm for ^1H NMR (400 MHz) and against $CDCl_3$ at 77.0 ppm for ^{13}C NMR (100 MHz, part of samples was characterized by 125 MHz NMR). Molecular weights and molecular weight distributions of the resultant copolymers were determined with a PL-GPC220 chromatograph (Polymer Laboratories) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with THF with 1.0 mL/min at 40 °C. The sample concentration was 0.4 wt %, and the injection volume was 100 μL. Calibration was performed using monodisperse polystyrene standards covering the molecular-weight range from 580 to 460 000 Da. Infrared spectra were recorded by using a Bruker Vector 22 FT-IR spectrophotometer. The glass transition temperature (T_g) of the resultant copolymer was determined by using a TA DSC-Q200 differential scanning calorimetry (DSC). The sample was heated in two cycles from room temperature to 80 °C at a rate of 5 °C/min in a nitrogen atmosphere. T_g was determined from the second run. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 instrument under a N_2 atmosphere at a heating rate of 10 °C/min from room temperature to 400 °C. Samples for thermal analyses were all purified. The refractive index (nD) was measured by Abbe

Table 1. *Rac*-PO/COS Copolymerization Results[a]



entry	catalyst	cocatalyst	TOF (h^{-1})[b]	copolymer selectivity[c]	PPMTC linkages (%)[c]	T-H linkages[d] (%)	O/S ER product[e]	M_n (kg/mol)[f]	PDI (M_w/M_n)[f]
1	**a**	[PPN]Cl	288	99/1	100	98.9	N.F.	24.4	1.26
2	**a**		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
3		[PPN]Cl	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
4	**b**	[PPN]Cl	310	99/1	100	99.0	N.F.	21.9	1.35
5	**c**	[PPN]Cl	332	99/1	100	98.6	N.F.	25.3	1.41
6[g]	**c**	[PPN]Cl	266	77/23	100	98.1	F	12.3	1.29
7[h]	**c**	[PPN]Cl	274	97/3	100	94.7	N.F.	6.6	1.06
8[i]	**c**	[PPN]Cl	290	98/2	100	95.2	N.F.	7.3	1.05
9[j]	**c**	[PPN]Cl	282	97/3	100	97.6	N.F.	7.5	1.07

[a]Reaction was performed in neat PO (2.0 mL, 28.6 mmol; catalyst/cocatalyst = 1/1, catalyst/PO = 1/1000, COS/PO = 2/1, all in molar ratio) in a 10 mL autoclave at 25 °C for 3.0 h. [b](Mol epoxide consumed)/(mol Cr h). [c]Determined by using ^1H NMR spectroscopy (Figure S1−5 in the Supporting Information). The polymer selectivity is the molar ratio of polymer **1**/cyclic product. The PPMTC linkages are the molar percentage of monothiocarbonate linkage in polymer chain. [d]Determined by using ^{13}C NMR spectroscopy. [e]Determined by using ^{13}C NMR spectroscopy. O/S ER = oxygen−sulfur exchange reaction. N.F. = not found and F = found. [f]Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [g]Reaction temperature was 60 °C. [h](*S*)-PO was used. [i](*R*)-PO was used. [j]75%(*S*)-PO/25%(*R*)-PO was used.

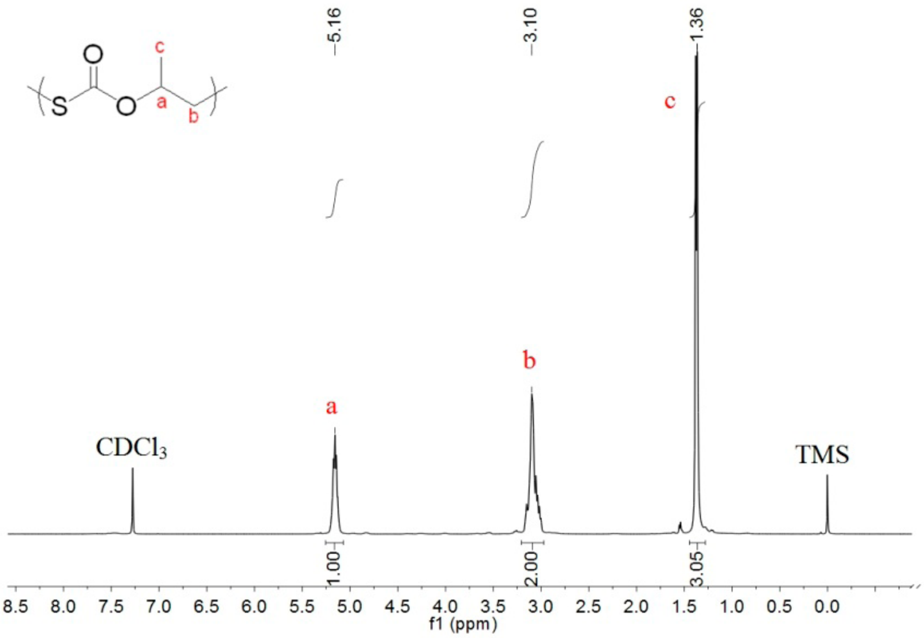


Figure 2. ^1H NMR spectrum of the crude product of entry 1 in Table 1.

refractometer. Electrospray ionization-tandem mass spectrometry (ESI−MS) analyses were performed on an Esquire3000 plus mass spectrometer using acetonitrile (CH_3CN) as a solvent for the copolymer. Raman spectra were recorded by using a RM2000 laser Raman spectrometer (powder sample, the measurement range was 100−4000 cm^{-1} resolution of 1 cm^{-1}). The catalysts (Salen)CrCl **a:** *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-benzenediamino chromium(III) chloride, **b:** *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediamino chromium(III) chloride, and **c:** (1*R*,2*R*) *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino chromium(III) chloride were synthesized according to the literature method.[11]

Copolymerization of PO with COS. The copolymerization of PO/COS was performed in a 10 mL autoclave equipped with a magnetic stirrer and a barometer. The (Salen)CrCl complex **a** (17.9 mg, 2.86×10^{-2} mmol), [PPN]Cl (16.43 mg, 2.86×10^{-2} mmol), and PO (2.00 mL, 28.6 mmol) were transferred into the autoclave, which was completely dried in advance. The autoclave was pressurized to the appropriate pressure with COS, and the reaction mixture was stirred at 25 °C for 3.0 h. After copolymerization, the autoclave was cooled and the pressure was slowly vented. The reaction mixture was dried in vacuum at 50 °C for isolating the unreacted reactants and weighed to calculate the TOF of the copolymerization. An aliquot was then taken from the resulting crude product for the determination of the ratio of copolymer **1**/cyclic product **1′** by ^1H NMR spectrum. After that, the crude product was dissolved in CH_2Cl_2 (10 mL) and precipitated from methanol (100 mL) three more times. Yellowish precipitate was collected and dried in vacuum at 70 °C to constant weight. The obtained copolymer was analyzed by ^1H NMR, ^{13}C NMR, FT-IR spectroscopy, and GPC. ^1H NMR ($CDCl_3$) δ 5.19−5.13 (m, 1H), 3.16−3.00 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.58, 73.45, 35.75, 19.01. [propylene monothiocarbonate **1′**: ^1H NMR ($CDCl_3$) 4.87−4.79 (m, 1H), 3.57−3.53 (m, 1H), 3.28−3.23 (m, 1H), 1.54 (d, J = 6.2 Hz, 3H)].

RESULTS AND DISCUSSION

Catalyst **a**/[PPN]Cl with a molar ratio of 1.0 was successfully applied to COS-PO copolymerization with a TOF of 288 (i.e.: PO conversion: 86.4%, entry 1 in Table 1). Blank reactions showed that **a** or [PPN]Cl did not solely catalyze COS−PO copolymerization (entries 2 to 3, Table 1). The selectivity of copolymer **1**/cyclic thiocarbonte was 99/1 based on the ^{1}H NMR spectrum (Figure 2). The alternating degree of the resultant copolymer **1** was estimated to be >99% because no ether units were observed from the ^{1}H NMR spectrum. No O/S ER had occurred, as confirmed by ^{13}C NMR spectrum (Figure S1c in the Supporting Information). One peak at 169.64 ppm was observed, which was ascribed to the carbon atom of monothiocarbonate linkage (−S(O)CO−, **1**).[7b,8a] Hence, the copolymer **1** was fully alternating and named poly(propylene monothiocarbonate) (PPMTC). The number-average molecular weight (M_n) of copolymer **1** was 24.4 kg/mol with a narrow PDI of 1.26.

Catalysts **b** and **c** could also catalyze COS-PO copolymerization in the presence of [PPN]Cl at 25 °C with high TOFs (entries 4 and 5 with TOFs of 310 and 332, respectively, Table 1). For the copolymer of entry 5, only one peak at 169.64 ppm was observed from ^{13}C NMR spectrum (curve A in Figure 3), which could be ascribed to −SC(=O)O− (**1** and/or **4**).[8a] However, when the COS/PO copolymerization was catalyzed by **c**/[PPN]Cl system at 60 °C (entry 6), considerable amounts of cyclic products (23 wt %) were collected, which were evident by the ^{13}C NMR and ^{1}H NMR spectra (curve B in Figure 3, Figure S4 in the Supporting Information) of the crude product. As seen in curve B in Figure 3, the products mentioned in Scheme 1 such as −SC(=O)S− (188.04 ppm, **3**), −OC(=O)O− (153.48 ppm, **2**), −SC(=O)O− (169.64 ppm, **1** and/or **4**), and cyclic byproducts of **3′** (197.59 ppm), **1′** and **4′** (172.59 ppm), and **2′** (154.92 ppm)[8a] were observed. Moreover, **4′** was confirmed by GC-MS technique (Figure S7 in the Supporting Information). These results indicated that the high reaction temperature will cause the occurrence of O/S ER and weaken the selectivity of the monothoicarbonate units.

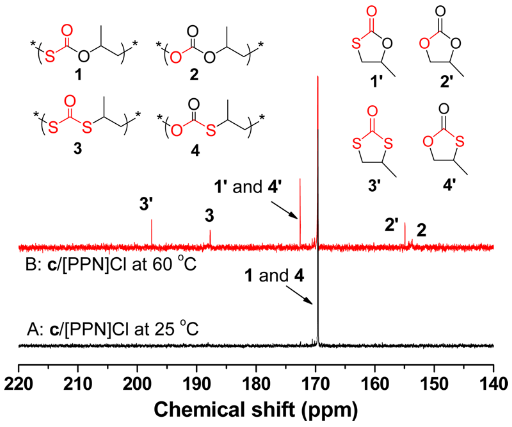
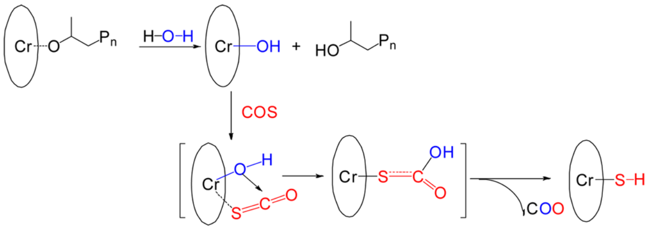


Figure 3. ^{13}C NMR spectra of carbonyl region of the crude products (entries 5 and 6 in Table 1). The formation of **1**−**4** and **1′**-**4′** is shown in Scheme 1 and Table S1 in the Supporting Information.

A series of COS/PO copolymerization were also investigated with various COS/PO molar ratios, solvents, and cocatalysts (Table S2 in the Supporting Information). The polymerization kinetics showed a linear increase in M_n with increasing reaction times (Figure S8 in the Supporting Information). The catalyst **c**/[PPN]Cl was proven to be the best binary catalyst for producing PPMTC with fully alternating degree and the complete depression of O/S ER.

The occurrence of O/S ER at 60 °C intrigued us to probe the structural change of the catalyst during the reaction. As previously mentioned, [Cr]−OH would be generated in our system via the chain transfer reaction. The produced [Cr]−OH could catalyze O/S ER in a proposed way, as shown in Scheme 2 and Scheme S2 in the Supporting Information. Such chain-transfer reaction can be accelerated by either increasing reaction temperature or introducing greater amounts of water (or compounds with active protons) into the system. Herein, the generation of CO_2 was confirmed by the observation of carbonate unit −OC(=O)O− and cyclic carbonate (curve B in Figure 3, Figures S4 and S7 in the Supporting Information), which may support the occurrence of chain-transfer reaction and the production of [Cr]−OH.

Scheme 2. Proposed Mechanism of the O/S ER during COS-PO Copolymerization



For further clarifying the structural change of (Salen)CrCl complex and following O/S ER induced by chain-transfer reaction during copolymerization, a series of control experiments were carried out by adding certain amounts of water to the reaction system, as shown in Table 2 (^{1}H and ^{13}C NMR spectra, see Figures S9−13 in the Supporting Information). When the molar ratios of H_2O/PO were 1/200 to 1/33, the TOFs, the selectivity, and the alternating degrees of the resultant copolymers remained nearly the same, while M_n of the resultant copolymers decreased clearly and PDI remained narrow. These phenomena were typical for the copolymerization with predominant chain-transfer reaction, which was similar to CO_2−PO copolymerization.[10,13] We also observed that O/S ER took place when the H_2O/PO molar ratio ≥1/50 (entries 3−5 in Table 2). The FT-IR (Figure S14 in the Supporting Information) and Raman (Figure S15 in the Supporting Information) spectra of the copolymer from entry 5 of Table 2 showed that it contained end −OH (3540 cm^{-1} in FT-IR) and −SH groups (2665 cm^{-1} in Raman spectrum). ESI-MS spectrum (Figure S16 in the Supporting Information) of this copolymer showed that it had three kinds of *m*/*z* species, which represented three copolymers of (i) H-PO-(COS-PO)$_n$-SH + Na$^+$, (ii) H-PO-(COS-PO)$_n$-OH + Na$^+$, and (iii) H-PO-(COS-PO)$_n$-(COS-PS)-SH+ Na$^+$ with relative abundance ratio of 100:18:7. No observation of copolymer with −Cl end group indicated that the chain-transfer reaction was very fast in the presence of considerable amounts of water.

The observation of copolymer with end −SH group confirmed the generation of [Cr]−SH, which initiated the COS−PO copolymerization. As a result, the transformation of [Cr]−Cl of (Salen)CrCl complex to [Cr]−OH, which could be converted to [Cr]−SH by O/S ER, was resulted from the

Table 2. *Rac*-PO/COS Copolymerization in the Presence of Various Amounts of Water[a]

entry	H_2O (μL)	H_2O:PO (molar ratio)	TOF[b] (h^{-1})	copolymer selectivity[c]	PPMTC linkages[c] (mol %)	T-H linkages[d] (%)	O/S ER product[e]	M_n[f] (kg/mol)	PDI[f] (M_w/M_n)
1	2.5	1/200	274	99/1	99	97.6	N.F.	9.5	1.12
2	5.0	1/100	282	99/1	99	97.1	N.F.	8.1	1.08
3	10.0	1/50	288	98/2	99	92.8	F	5.2	1.06
4	15.0	1/33	266	90/10	98	90.9	F	3.9	1.06
5	30.0	1/17	157	86/14	86	76.0	F	1.2	1.15

[a] Reaction was performed in neat PO (2.0 mL, 28.6 mmol; **a**/[PPN]Cl = 1/1, catalyst/PO = 1/1000, COS/PO = 2/1, all in molar ratio) in a 10 mL autoclave at 25 °C for 3.0 h. [b] (Mol epoxide consumed)/(mol Cr h). [c] Determined by using ^{1}H NMR spectroscopy (Figures S9−13 in the Supporting Information). The polymer selectivity is the molar ratio of polymer **1**/cyclic product. The PPMTC linkages are the molar percentage of monothiocarbonate linkage in polymer chain. [d] Determined by using ^{13}C NMR spectroscopy (Figure S9−13 in the Supporting Information). [e] Determined by using ^{13}C NMR spectroscopy (Figure S9−13 in the Supporting Information). O/S ER = oxygen−sulfur exchange reaction. N.F. = not found and F = found. [f] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards.

chain-transfer reaction (Scheme S2 in the Supporting Information).

Under the premise of the complete depression of O/S ER, the stereochemistry of COS-PO copolymerization can be clarified. The units of −OC(=S)O− (**5**), −SC(=S)O− (**6**), and corresponding cyclic products of **5′** and **6′** were not observed in ^{13}C NMR spectra of all copolymers listed in Tables 1 and 2. It indicated that the insertion path **B** in Scheme 1 was totally prohibited. That is, the coordination of the sulfur atom of COS to the active center was completely selective. As a result, only one propagating species (−OC(=O)S$^-$, via route **A**) existed before PO insertion. The nucleophilic attack of −OC(=O)S$^-$ to CH_2 or CH of PO determines the regioregularity of the resultant copolymer (Scheme 1 and Scheme S3 in the Supporting Information).

It seems hard to accurately assign the multiple peaks of −SC(=O)O− unit [curve (A), Figure 4] to the various microstructures (i.e., H−T, T−H, T−T, and H−H diads) of the copolymer **6** (entry 6, Table 1). If the cyclic monothiocarbonate could be predominantly generated via the backbiting from the anionic alkoxy−chain end,[10] as shown in Scheme 3, then the molar ratio of cyclic monothiocarbonates **1′** to **4′** could represent the molar ratio of the units −OC(=O)$SCH_2CH(CH_3)O$− to −OC(=O)$SCH(CH_3)CH_2O$− in the copolymer. GC-MS measurements were then carried out to clearly differentiate **1′** and **4′**, and the diads of the copolymer could be deduced. The GC-MS results showed that the molar ratio of cyclic monothiocarbonates **1′** to **4′** was 40 for the system of entry 6 in Table 1, as shown in Figure S7 in the Supporting Information, indicating that the −OC(=O)S CH_2CH $(CH_3)O$− unit was the main structure of the copolymer even if O/S ER had occurred. Furthermore, the content of T−H diad of copolymer **6** was estimated to be 97.6% from the molar ratio of **1′**/(**1′** + **4′**), which was consistent with that of 98.1% calculated from ^{13}C NMR spectrum (entry 6 in Table 1). The multiple peaks at 169.64 ppm could be then assigned to the T-H diad. The content of T-H diad in all copolymers in Table 1 was calculated as 98.1 to 99.0%, indicating that the copolymerization was highly regioselective.

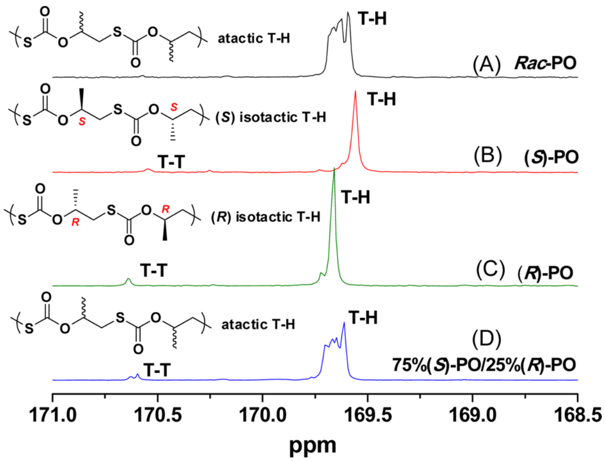


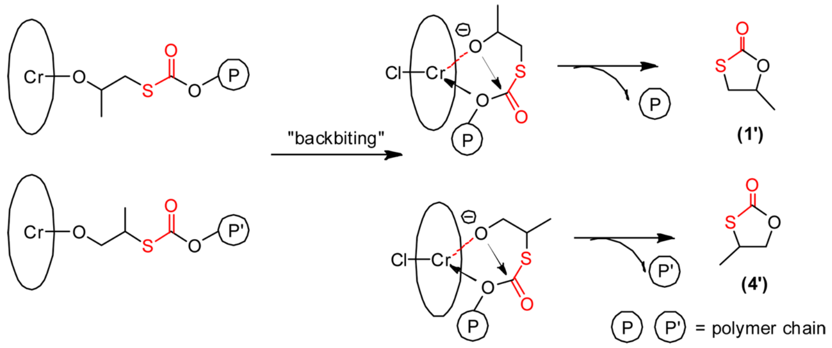
Figure 4. Carbonyl region of the ^{13}C NMR spectra of PPMTC resulted from (A) *rac*-PO/COS (entry 6, Table 1) and (B) (*S*)-PO/COS (entry 7, Table 1); (C) (*R*)-PO/COS (entry 8, Table 1) and (D) 75%(*S*)-PO/25%(*R*)-PO/COS (entry 9, Table 1). Note that (*S*)-PO, (*R*)-PO, and 75%(*S*)-PO/25%(*R*)-PO were used without further purification.

For further demonstrating the unique regioregularity of PPMTC, (*S*)-PO, (*R*)-PO, and 75%(*S*)-PO/25%(*R*)-PO were copolymerized with COS by using the catalyst **c**/[PPN]Cl (entries 7−9, Table 1). Note that (*S*)-PO, (*R*)-PO, and 75%(*S*)-PO/25%(*R*)-PO were used without further purification. The (*S*) [or (*R*)]-configuration of methine carbon of (*S*) [or (*R*)]-PO was expected to be retained after copolymerization if just **a**−**a** propagating manner took place. Hence, the isotactic T−H diad would be the only configuration of the resultant copolymer and will cause one single peak in its ^{13}C NMR spectrum. This expectation was proved by the ^{13}C NMR spectrum of COS/(*S*)-PO copolymer and COS/(*R*)-PO copolymer, as shown in curves (B) and (C) in Figure 4. Moreover, the copolymer from COS with 75% (*S*)-PO/25% (*R*)-PO presented similar multiple peaks as those observed for *rac*-PO/COS copolymer [curve (A), Figure 4], and the sharp peak at right-hand [(*S*) isotactic T-H diad, curve (D)] became relative stronger because of greater amounts of (*S*)-PO in the system.

The obtained PPMTC is highly soluble in common solvents, such as, CH_2Cl_2, $CHCl_3$, and THF. The glass-transition temperature (T_g) of PPMTC of entry 7 in Table 1 was 22.4 °C (Figure S17 in the Supporting Information). Interestingly, the initial decomposition temperature of this copolymer was 137 °C and rather low (Figure 5). Refractive index (*n*D) of this copolymer was measured to be 1.63(22 °C, cast film), which can be classified into polymers with large refractive index. Such low decomposition temperature and high refractive index of PPMTC make it a potential scarifying optical adhesive.

In conclusion, the regioselective and alternating copolymerization of COS and PO are reported for the first time using the binary (Salen)CrCl/[PPN]Cl catalyst system. The O/S ER

Scheme 3. Proposed Production of Cyclic Monothiocaarbonate 1′ and 4′ by "Backbiting" Mechanism



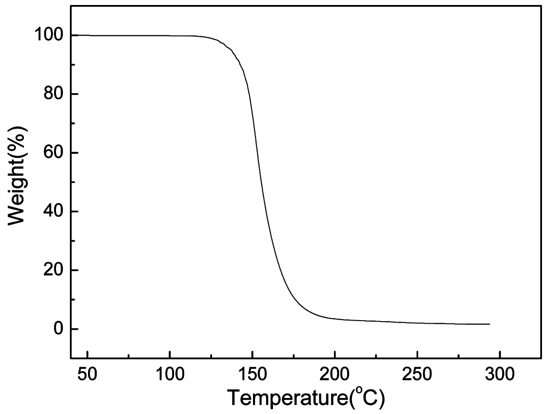


Figure 5. TGA curve of the COS-PO copolymer (entry 1, Table 1).

could be completely inhibited at 25 °C. The resultant copolymers had 98.1 to 99.0% T−H linkages and full alternating asymmetric monothiocarbonate units. Importantly, it also presented a new copolymerization model involved two asymmetric monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and tables giving general experimental procedures and characterization data for PO−COS copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Torres, A. L.; Maroulis, P. J.; Goldberg, A. B.; Bandy, A. R. *J. Geophys. Res., C: Oceans Atmos.* **1980**, *85*, 7357−7360.

(2) (a) Svoronos, P.; Bruno, T. J. *Ind. Eng. Chem. Res.* **2002**, *41*, 5321−5336. (b) Rhodes, C.; Riddel, S. A.; West, J.; Williams, B. P.; Hutchings, G. J. *Catal. Today* **2000**, *59*, 443−464.

(3) (a) Yokota, H.; Kondo, M. *J. Polym. Sci., Part A: Polym.Chem.* **1971**, *9*, 13−25. (b) Stephen, Y.; Osborn, W. U.S. Patent *3,213,108*, 1965.

(4) (a) Lu, X.-B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462−1484. (b) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388−2410. (c) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618−6639.

(5) (a) Ochiai, B.; Endo, T. *Prog. Polym. Sci.* **2005**, *30*, 183−215. (b) Marianucci, E.; Berti, C.; Pilati, F.; Manaresi, P.; Guaita, M.; Chiantore, O. *Polymer* **1994**, *35*, 1564−1566.

(6) (a) You, Y.-Z.; Hong, C.-Y.; Pan, C.-Y. *Macromol. Rapid Commun.* **2002**, *23*, 776−780. (b) Leung, L. M.; Chan, W. H.; Leung, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1799−1806. (c) Berti, C.; Marianucci, E.; Pilati, F. *Macromol. Chem. Phys.* **1988**, *189*, 1323−1330.

(7) (a) Ochiai, B.; Yoshii, K.; Nagai, D.; Endo, T. *J. Polym. Sci., Part A: Polym.Chem.* **2005**, *43*, 1014−1018. (b) Nemoto, N.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 7229−7231. (c) Choi, W. M.; Sanda, F.; Endo, T. *Macromolecules* **1998**, *31*, 2454−2460.

(8) (a) Darensbourg, D. J.; Andreatta, J. R.; Jungman, M. J.; Reibenspies, J. H. *Dalton Trans* **2009**, 8891−8899. (b) Zhang, X.-H.; Liu, F.; Sun, X.-K.; Chen, S.; Du, B.-Y.; Qi, G.-R.; Wan, K.-M. *Macromolecules* **2008**, *41*, 1587−1590. (c) Nakano, K.; Tatsumi, G.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 15116−15117.

(9) (a) Schenk, S.; Notni, J.; Kohn, U.; Wermann, K.; Anders, E. *Dalton Trans* **2006**, 4191−4206. (b) Schenk, S.; Kesselmeier, J.; Anders, E. *Chem.—Eur. J.* **2004**, *10*, 3091−3105.

(10) Darensbourg, D. J. *Inorg. Chem.* **2010**, *49*, 10765−10780.

(11) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C.-C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024−6034.

(12) Li, B.; Zhang, R.; Lu, X.-B. *Macromolecules* **2007**, *40*, 2303−2307.

(13) Zhang, X.-H.; Wei, R.-J.; Sun, X.-K.; Zhang, J.-F.; Du, B.-Y.; Fan, Z.-Q.; Qi, G.-R. *Polymer* **2011**, *52*, 5494−5502.

The United States of America

The Director of the United States Patent and Trademark Office

Has received an application for a patent for a new and useful invention. The title and description of the invention are enclosed. The requirements of law have been complied with, and it has been determined that a patent on the invention shall be granted under the law.

Therefore, this

United States Patent

Grants to the person(s) having title to this patent the right to exclude others from making, using, offering for sale, or selling the invention throughout the United States of America or importing the invention into the United States of America, and if the invention is a process, of the right to exclude others from using, offering for sale or selling throughout the United States of America, or importing into the United States of America, products made by that process, for the term set forth in 35 U.S.C. 154(a)(2) or (c)(1), subject to the payment of maintenance fees as provided by 35 U.S.C. 41(b). See the Maintenance Fee Notice on the inside of the cover.

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(12) **United States Patent**
Zhang et al.

(10) **Patent No.: US 8,859,452 B2**
(45) **Date of Patent: Oct. 14, 2014**

(54) METAL CYANIDE COMPLEX CATALYST AND ITS PREPARATION AND APPLICATION

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USPC 502/175, 201, 217, 224
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,500,704 A 2/1985 Kruper, Jr. et al.
4,826,053 A 5/1989 Keller

(Continued)

FOREIGN PATENT DOCUMENTS

CN 1740208 A 3/2006
CN 101003622 A 7/2007

(Continued)

OTHER PUBLICATIONS

Sun, Xueke, et al., Alternating Copolymerization of Carbon Dioxide and Cyclohexene Oxide Catalyzed by Silicon Dioxide/Zn-CoIII Double Metal Cyanide Complex Hybrid Catalysts with a Nanolamellar Structure, Journal of Polymer Science: Part A: Polymer Chemistry, vol. 46, 2008, pp. 3128-3139.

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(57) ABSTRACT

A metal cyanide complex catalyst and its preparation and application are disclosed. The formula of this catalyst is $M^1_a[M^2(CN)_bL1_c]_d(X)_m(L2)_n.xSu.yL3.zH_2O$ and its preparation method comprises: (A) adjusting pH of a mixed solution I' of L3, $M^3_e[M^2(CN)_bL1_c]_f$, de-ionized water I, alcohol and/or ether solvent to less than 7.0, and adding it into a mixed solution II' of $M^1(X)_g$ salt, Su or Su precursor, de-ionized water II, stirring for reaction under 20° C.-120° C. for 0.5-200 hours, separating and drying to obtain a solid product; and (B) repeatedly dispersing the solid into an anhydrous organic solvent containing L2 to form a slurry, distilling, separating and drying to obtain the metal cyanide complex catalyst. The catalyst is useful in preparing polyethers, polycarbonates and polyesters by homopolymerization of epoxides, or copolymerization of epoxides with carbon dioxide or anhydrides.

7 Claims, 3 Drawing Sheets

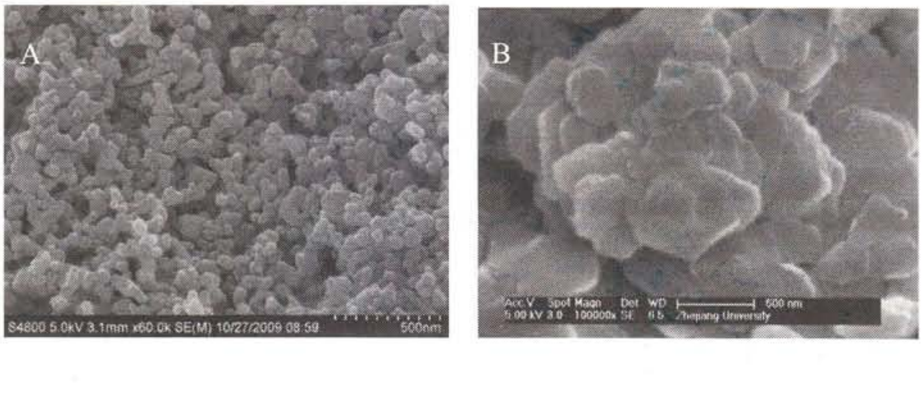

TABLE 3

The terpolymerization of two epoxides and CO2

No.	temperature (° C.)	pressure (MPa)	epoxide 1 (mL)	epoxide 2 (mL)	catalytic activity	content of cPC (%)	alternative degree	M_w (10^{-4})	PDI
15	75	4.0	CHO/5	VCHO/15	1230	0	94.4	13.5	2.5
16	50	5.0	CHO/5	PO/45	1400	<2	91.8	8.5	2.0
17	60	4.0	CHO/7	PO/60	1550	<2	95.0	10.5	1.9
18	70	4.0	CHO/7	PO/60	1300	<2	93.0	8.5	2.2
19	50	4.0	CHO/10	PO/60	1344	<1	94.0	10.9	2.2
20	50	6.0	CHO/7	PO/60	1480	<1	98.0	20.6	2.4

T_gs of Nos. 16, 17, 18, 19 and 20 in Table 3 are 42.3° C., 41.2° C., 43.6° C., 44.4° C. and 44.7° C., respectively (DSC method, 10° C./min, taken from the thermal transition of the second curve), see curves 2~6 in FIG. **6**. ^{1}HNMR spectrum of the crude terpolymer of CO_2/PO/CHO in No. 20 was shown in FIG. **5**. The chemical shifts at 4.9 ppm and 4.4 ppm are ascribed to the methine and methylene protons of propylene carbonate unit and cyclohexene carbonate unit, while 4.5 ppm and 3.5~3.7 ppm are ascribed to the methine protons of cyclic carbonate and methylene and methine protons of ether unit, respectively. As shown in Table 1, the intensity of peaks at 4.5 ppm and 3.5~3.7 ppm is rather low, suggesting the contents of cyclic carbonate byproduct and polyether in the crude product was also rather low.

Example 11

The catalyst employed in this example was prepared according to Example 1. Step polymerization was adopted for epoxides homopolymerization in this example.

7.0 mg of catalyst and 20 g of starting material (PPG-400) were added into a 500-mL stainless steel autoclave reactor, then the reactor was heated to 110° C. and N_2-vacuum cycle was carried out repeatedly for removing the trace water for 0.5 hours. After the autoclave was further heated to 120° C., PO (10 mL) was injected into autoclave using a metering pump. After the pressure of the system decreased dramatically (18 minutes), PO monomer (100 mL) was injected into autoclave in batches with 10 mL PO for each time within 5 h. After the reaction, the pressure was reduced to remove the remaining monomer. A viscous liquid product was then obtained.

M_n=3.8 kDa, PDI=1.08. The percentage of the product with M_n>100 kDa in the final product was below 500 ppm, while those of PO ROP catalyzed by traditional DMC catalyst was generally >1000 ppm.

The catalytic activity was 51.5 kg polyether/g catalyst.

Example 12

The catalyst employed in this example was prepared according to Example 4. The catalyst was adopted for epoxides/anhydride copolymerization in this example.

Prior to polymerization reaction, a 60-mL autoclave was dried under vacuum at 110° C. for 2 hours for removing trace water, and cooled to room temperature in the drying tower. 3.0 mg of the catalyst, 2.0 g of maleic anhydride, 4 mL of cyclohexene oxide and 4.0 mL of tetrahydrofuran were added into the autoclave. The reactor was sealed and then heated in an oil bath to a temperature of 90° C. for reaction for 5 hours with magnetic stirring. After the reaction, the autoclave was rapidly cooled down and the pressure was vented. Crude product was removed. The pressure was reduced and solvents were removed, then the crude product was solved in THF and precipitated by methanol, then dried under vacuum to obtain a yellow product, which was weighed to calculate the conversion. The content of polyether unit and polyester unit was calculated from ^{1}HNMR spectrum.

M_n=24,000, PDI=1.6. Alternative degree: 96%. The final catalytic activity was 3.2 kg polyether/g catalyst. The glass transition temperature is 82° C.

Example 13

The catalyst employed in this example was prepared according to Example 4. The catalyst was adopted for epoxides/anhydride/CO_2 terpolymerization in this example.

Prior to polymerization reaction, a 100-mL autoclave was dried under vacuum at 110° C. for 2 hours for removing trace water. 10.0 mg of catalyst, 4.0 g of maleic anhydride, 40 mL of cyclohexene oxide and 40 mL of tetrahydrofuran were sequentially added into the autoclave. The reactor was sealed. CO_2 was added to a desired pressure of 4.0 MPa. The reaction was performed for 5 h with stirring. After the reaction, the autoclave was rapidly cooled down and pressure was vented. Crude products were removed. The products were dissolved with methylene dichloride and precipitated by methanol, then the yellow products were dried under vacuum. The conversion was calculated from weight of the products. The content of polyether unit and polyester unit was calculated from ^{1}HNMR spectrum.

M_n=30,000, PDI=1.8. Alternative degree was 98%. The final catalytic activity was 5.6 kg polyether/g catalyst. The glass transition temperature is 108° C.

The invention claimed is:

1. A process for preparing a metal cyanide complex catalysts comprising the following steps:

step 1: a solution I' is prepared by mixing a cyanide metal salt of formula (2) into a mixture of L3, de-ionized water I, alcohol and/or ether solvents, and the pH value of the solution I' is then adjusted to less than 7.0; a solution II' is comprised of $M^1(X)_g$ salt, Su or Su precursors, de-ionized water II; the solution I' and the solution II' are then mixed by adding the solution I' into the solution II' under stirring at 0~120° C. for 0.5~200 hour, the resultant precipitate is separated and dried,

$$M^3_e[M^2(CN)_bL1_c]_f \quad (2)$$

wherein, M^3 is an alkali metal ion, alkali earth metal ion or hydrogen ion, e and f are positive numbers, M^2, L1, b, and c are the same as (1) described below,

wherein, L3, M^1, X and Su are the same as in formula (1), g is 1 or 2,

in the mixed solution I', molar ratio of the cyanide metal salt of formula (2) and de-ionized water I is 0.005-2 g/mL, the weight ratio of L3 and de-ionized water I is 0~40%, the volume fraction of alcohol and/or ether with the de-ionized water I is 0~2, in the mixed solution II", molar ratio of $M^1(X)_g$ salt/de-ionized water II is 0.05~1 g/1 mL, molar ratio of the cyanide metal salt of formula (2)/$M^1(X)_g$ salt is 1/1~50, mass ratio of the cyanide metal salt of formula (2) and Su (or Su precursor) is 1/0~20,

step 2: solid product prepared from step 1 is dissolved and reslurried in an anhydrous organic solvent containing L2 for several times, molar ratio of L2/the cyanide metal salt of formula (2) is 0.1~10, slurry temperature is 20~120° C., and slurry time is 0.5~200 h, slurry action being under an inert atmosphere or closed reactive vessel, then the metal cyanide complex catalyst is obtained by a distillation, separation and drying processes; wherein the metal cyanide complex catalyst has the formula:

$$M^1_a[M^2(CN)_bL1_c]_d(X)_m(L2)_n.xSu.yL3.zH_2O \quad (1)$$

wherein,

M^1 is a divalent metal ion, which is selected from one of Zn^{2+}, Co^{2+}, Ni^{2+} or Fe^{2+};

M^2 is a divalent or trivalent metal ion (not including Fe^{2+} or Fe^{3+}), which is selected from one of Co^{3+}, Ni^{2+}, Cd^{2+}, Cr^{3+} or Mn^{3+};

L1 is an internal ligand which coordinates with M^2, it is selected from one or two of mono-dentate ligands with N, O, P or S as a coordinate atom, bi-dentate ligands with O, S, P or N as a coordinate atom or halide anions;

X is an anion selected from one or more of F^-, Cl^-, Br^-, I^-, OAc^-, SO_4^{2-}, NO_3^-, aryloxy anions, and organic carboxylic ions;

L2 is an electron-donating neutral ligand with N, O, P and S as a coordinated atom, and coordinated with M^1;

Su is selected from one or more of halides, sulfates and nitrates of the IIA and IIIA group metal elements, lithium halide salts, silicon dioxide, titanium dioxide;

L3 is a water-soluble polymer, a polymer that can self-assembly in a mixed solution of water and alcohol, or a mixed solution of water and ether, or a mixed solution of water, alcohol and ether;

a and d are positive numbers, b is positive integer, c is 0, 1 or 2, m and n are positive numbers, x, y and z are zero or positive numbers, and a:d=1~4, a:n=0.001~5.

2. The process according to claim **1**, wherein molar ratio of the cyanide metal salt of formula (2)/$M^1(X)_g$ salt is 1/1~30 in step 1.

3. The process according to claim **1**, wherein the volume fraction of alcohol and/or ether with the de-ionized water I in mixed solution I' is 0~0.8 in step 1.

4. The process according to claim **1**, wherein the slurry temperature is 40~100° C. in step 2.

5. The process according to claim **1**, wherein in step 2, the anhydrous organic solvent containing L2 and $M^1(X)_g$ salt, the molar ratio of $M^1(X)_g$ salt to cyanide metal salt of formula (2) is 0~2.

6. The metal cyanide complex catalysts are described according to claim **1**, wherein the electron-donating neutral ligand L2 is selected from the group consisting of N-alkyl imidazoles, N-aryl imidazoles, bipyridyl, pyridine, aliphatic nitriles, aromatic nitriles, N,N'-dialkyl amides, N,N'-diaryl amides, N-substituted cyclic amides, sulfoxide or sulfone compounds, organic carboxylates, ketones, cyclic ketones, phosphates, all alkyl-substituted cyclotriphosphazenes, full-aryl-substituted cyclotriphosphazenes, carbonates, cyclic lactones, thioethers, cyclic carbonates or cyclic ethers.

7. The metal cyanide complex catalysts are described according to claim **1**, wherein their shape is nano lamellar or nano spherical, and they have nanopores with an average diameter of less than 100 nm.

* * * * *