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CO_2/顺式-2,3-环氧丁烷交替共聚物的立体寡聚物合成及微结构分析

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摘要 聚合物主链的立体结构与其热力学性能密切相关. 精确控制聚合物立体化学是配位聚合催化最重要的研究目标之一, 而合成确定分子量的各种立构规整性寡聚物和它们的核磁碳谱分析是精确表征聚合物微结构的关键. 本研究以手性2,3-丁二醇为起始原料, 通过迭代合成方法, 采用三光气为羰化试剂, 制备了全同和间同结构的CO_2/顺式-2,3-环氧丁烷交替共聚物(聚碳酸-2,3-丁烯酯)的四聚体和八聚体, 并从它们的碳谱信息精确分析聚碳酸-2,3-丁烯酯的微结构. 发现全同聚合物的羰基、次甲基和甲基的核磁碳谱分别对应于154.12、75.23和15.71 ppm化学位移处, 而间同结构聚碳酸酯的羰基、次甲基和甲基的核磁碳谱分别对应于154.09、75.07和15.51 ppm.

关键词 CO_2, 聚碳酸酯, 寡聚物, 微结构分析, 核磁共振碳谱

聚合物的物理性质与其主链立体结构之间存在很大的相关性[1]. 例如, 全同和间同聚丙烯都是典型的半结晶材料, 熔点分别在170和160°C左右, 然而无定形聚丙烯是一种非结晶性聚合物, 其玻璃化转变温度低于0°C. 对于如聚乳酸等可生物降解聚合物而言, 全同结构的降解速率远慢于无定形聚合物, 这是由于全同聚合物中构筑单元的有序排列导致的紧凑密堆积结构[2]. 所以, 聚合物微结构的精确控制是配位聚合催化领域的重要研究目标之一[3]. 此外, 由于聚合物链中相邻位置的相对立体化学保留了反应路径的痕迹[4], 因此, 聚合物链的立体化学信息归属对于理解聚合机理和进一步设计更具活性和高立构规整性的催化体系具有重要意义.

自从Inoue等人[5]于1969年首次报道了环氧烷烃与CO_2交替共聚生成可降解性聚碳酸酯反应以来, 化学家开发出许多用于该共聚反应的催化体系[6~15]. 其中, 基于金属-salen配合物的二元或双功能催化剂呈现高活性和优异的区域和立体选择性, 使用的金属中心主要包括铬[16~20]、钴[20~29]和锌[20,30~32]等. 伴随着这些立构规整性催化剂的开发, 还相继报道了关于环氧烷烃开环的区域化学和碳酸酯单元序列的立体化学研究[33~36]. 2004年, Chisholm等人[33,34]合成了一系列聚碳酸丙烯酯的模型化合物, 通过其^{13}C NMR和^{1}H NMR研究发现在二聚体和四聚体化合物上羰基碳的信号会受到它相邻的环氧丙烷开环单元的区域和立体化学的影响. 2012年, Rieger课题组[35]利用手性气相色谱和高分辨核磁共振波谱研究了不同聚碳酸丙烯酯的微结构, 通过分析不同聚合条件下制备的共聚物微结构, 推测该聚合反应依照双金属共聚机理进行. 2013年, 本课题组[36]合成了具有尾-尾、头-尾和头-头3种连接单元的聚碳酸苯乙烯酯二聚体的9种构型化合物, ^{13}C NMR研究分析表明全同和间同二聚体能较好归属先前研究的

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Luo J, Sun X Y, Wang X D, et al. Synthesis and microstructure analysis of stereoregular oligomers of CO_2/*cis*-2,3-butene oxide alternating copolymer (in Chinese). Chin Sci Bull, 2020, 65: 3418–3428, doi: 10.1360/TB-2020-0320

聚碳酸苯乙烯酯的立体微结构信息[37].

与端位环氧烷烃和二氧化碳共聚物的微结构研究相比, 内消旋环氧烷烃与二氧化碳的交替共聚物的微结构研究受到较少的关注[38,39]. 2001年, Nozaki课题组[38]采用逐步合成的方法(图1), 制备出聚碳酸环己烯酯的寡聚物, 完成了聚碳酸环己烯酯的微结构归属, 发现全同立构序列的羰基碳核磁信号出现在153.7 ppm (parts per million)处, 间同立构序列的出现在153.3~153.1 ppm处. 2006年, Coates课题组[39]使用伯努利统计方法, 归属出聚碳酸环己烯酯在^{13}C NMR中的四元和三元序列. 2015年, 本课题组[40]合成了聚碳酸环戊烯酯的全同和间同二聚寡聚物(图2), 并对其进行^{13}C NMR表征, 153.85 ppm处的核磁信号归属为全同立构序列的羰基碳, 153.78 ppm处为间同结构的羰基碳.

本研究以手性2,3-丁二醇为起始原料, 通过迭代合成方法, 采用三光气为羰化试剂, 制备了全同和间同结构的CO_2/顺式-2,3-环氧丁烷交替共聚物(聚碳酸-2,3-丁烯酯)的四聚体和八聚体, 并通过^{13}C NMR分析, 期望实现聚碳酸-2,3-丁烯酯的各种立体结构归属.

1 实验

(ⅰ) 测试仪器. ^{1}H NMR(400 MHz): Varian INOVA-400 MHz, 以四甲基硅烷作为内标(0 ppm), 溶剂为氘代氯仿($CDCl_3$). ^{13}C NMR(125 MHz): Bruker 500 MHz, 溶剂为$CDCl_3$.

(ⅱ) 原料、试剂及纯化. (*R*,*R*)-(-)-2,3-丁二醇((*S*,*S*)-**1**), (*S*,*S*)-(+)-2,3-丁二醇购自浙江泽天精细化工有限公司, *ee*>98%. N_2购自大连光明特种气体研究所. 柱层析用硅胶购自青岛市麦克硅胶干燥剂有限公司. 氢氧化钾、吡啶(纯度98%)、三乙胺购自天津市大茂化学试剂厂. 三乙胺使用前需要做蒸馏精制处理: 氮气保护下, 加入干燥剂氢化钙搅拌, 加热回流24 h, 常压蒸出并存放在储液瓶中备用. 叔丁基二甲基硅基三氟甲磺酸酯(纯度98%)、三氟化硼乙醚溶液(纯度98%, 浓度46.5%)、

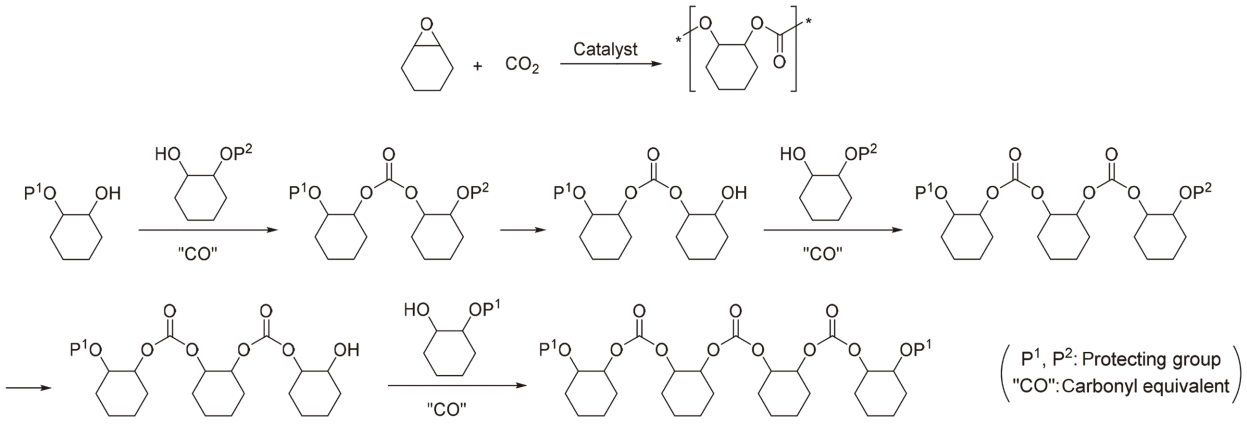

图 1 (网络版彩色)用于研究聚碳酸环己烯酯微结构的模型寡聚物的合成策略
Figure 1 (Color online) Synthetic strategy of model oligomers for studying the microstructure of poly(cyclohexene carbonate)s

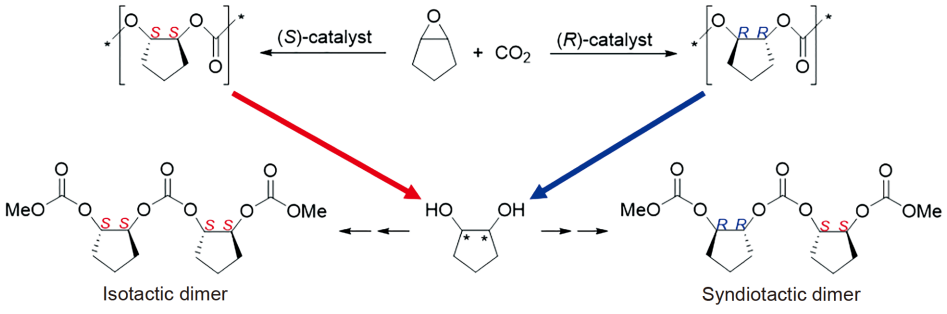

图 2 (网络版彩色)用于研究聚碳酸环戊烯酯微结构的二聚体的合成
Figure 2 (Color online) Synthesis of dimer for studying the microstructure of poly(cyclopentene carbonate)s

钯碳催化剂(质量分数10%)、三光气(纯度99%)购自萨恩化学技术有限公司. 溴化苄(纯度98%)、4-氟苯硼酸(纯度99%)、四乙基溴化铵(纯度99%)、*N*,*N*′-羰基二咪唑(纯度98%)、氢化钠(纯度60%, 分散于液状石蜡)购自北京伊诺凯科技有限公司. 4-二甲氨基吡啶(分析纯)购自武汉瑞基化工有限公司. 氯甲酸甲酯(分析纯)购自联华科技有限公司. 常规的溶剂都是市场购买的化学纯试剂, 使用之前需要经过合适的精制方法精制后置于储液瓶备用.

(ⅲ) 合成方法. 合成中所使用的玻璃仪器均经110°C干燥3 h以上.

(*S*,*S*)-**2**的合成: 氮气保护下, 将(*S*,*S*)-**1**(60.0 g, 665.8 mmol)和185 mL无水三乙胺溶于800 mL无水二氯甲烷中, 搅拌冷却至0°C, 滴加叔丁基二甲硅基三氟甲磺酸酯(158.2 g, 599.2 mmol)保持0°C搅拌反应8 h. 加入400 mL饱和碳酸氢钠溶液淬灭反应, 分相, 有机相用200 mL饱和氯化钠溶液洗涤, 分出有机相, 无水硫酸钠干燥. 旋干溶剂, 得未经分离的67.9 g(*S*,*S*)-**2**粗产物, 为无色油状液体. HRMS(*m*/*z*): Calcd. for $[C_{10}H_{25}O_2Si]^+$: 205.1618, found: 205.1619.

(*S*,*S*)-**3**的合成: 氮气保护下, 将(*S*,*S*)-**1**(40.0 g, 443.9 mmol)、溴化苄(151.2 g, 887.8 mmol)、4-氟苯硼酸(6.2 g, 44.4 mmol)、四乙基溴化铵(92.8 g, 443.9 mmol)和氢氧化钾(24.8 g, 443.9 mmol)投入三口烧瓶中, 加入700 mL甲苯, 35°C 搅拌反应36 h. 恢复室温后将反应液倒入300 mL水中, 乙酸乙酯萃取, 振荡后静置分相, 有机相用无水硫酸钠干燥. 减压旋蒸除去溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得40.0 g (*S*,*S*)-**3**. 产物为红棕色油状液体, 产率50%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.42~7.27(m, 5H), 4.56(dd, *J*=90.7, 11.5 Hz, 2H), 3.69~3.56(m, 1H), 3.32(m, 1H), 1.17(t, *J*=5.9 Hz, 6H). HRMS(*m*/*z*): Calcd. for $[C_{11}H_{17}O_2]^+$: 181.1223, found: 181.1223.

(*S*,*S*)-**4**的合成: 氮气保护下, 将未经纯化分离的(*S*,*S*)-**2**(67.9 g)和1,8-二氮杂二环十一碳-7-烯(3.7 g, 24.5 mmol)溶于700 mL无水二氯甲烷中, 缓慢加入*N*,*N*′-羰基二咪唑(170.0 g, 1048.4 mmol), 室温下搅拌反应6 h. 将反应液缓慢加入100 mL水中, 再边搅拌边加入1 mol/L盐酸, 将pH调为酸性, 静置分相, 分离出的有机相用无水硫酸钠干燥. 减压旋蒸除去溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得37.5 g (*S*,*S*)-**4**. 产物为红棕色油状液体. ^{1}H NMR(400 MHz, $CDCl_3$) δ8.12(s, 1H), 7.41(s, 1H), 7.06(s, 1H), 5.07~4.93(m, 1H), 3.98~3.86(m, 1H), 1.34(d, *J*=6.5 Hz, 3H), 1.18(d, *J*=6.3 Hz, 3H), 0.84(s, 9H), 0.07(s, 6H). ^{13}C NMR(125 MHz, $CDCl_3$) δ71.49, 26.00, 18.20, 16.47, −4.47, −4.58.

Iso-**2**-I的合成: 氮气保护下, (*S*,*S*)-**3**(20.0 g, 111.0 mmol)和60wt%氢化钠(5.3 g, 133.2 mmol)溶于200 mL无水四氢呋喃中, 室温搅拌6 h, 得到混合液. 氮气保护下, (*R*,*R*)-**4**(34.8 g, 116.7 mmol)溶于200 mL无水四氢呋喃中, 将混合液滴入其中, 室温搅拌反应1 h. 将反应液缓慢倾倒入250 mL 1 mol/L盐酸中, pH调为酸性, 减压旋蒸除去四氢呋喃, 加入400 mL二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(20:1, 体积比)作洗脱剂柱层析, 得42.2 g *Iso*-**2**-I. 产物为淡黄色油状液体, 产率93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.36~7.23(m, 5H), 4.88(m, 1H), 4.70~4.62(m, 1H), 4.64~4.51(m, 2H), 3.85(m, 1H), 3.62 (m, 1H), 1.26(d, *J*=6.5 Hz, 3H), 1.18(dd, *J*=6.4, 1.2 Hz, 6H), 1.12(d, *J*=6.3 Hz, 3H), 0.88(s, 9H), 0.07(s, 6H). ^{13}C NMR(100 MHz, $CDCl_3$) δ154.72, 138.73, 128.42, 127.69, 127.61, 78.00, 76.11, 76.04, 71.41, 69.64, 25.90, 18.74, 18.13, 15.29, 15.16, 14.96, −4.54, −4.77.

Iso-**2**-II的合成: 将*Iso*-**2**-I(16.0 g, 39.0 mmol)和Pd/C (10wt%, 0.8 g)加入高压釜中, 用乙醇溶解. 高压釜密封好后通入氢气(0.1 MPa), 室温搅拌反应24 h. 过滤除去Pd/C, 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得12.6 g *Iso*-**2**-II. 产物为无色油状液体, 产率99%. ^{1}H NMR(400 MHz, $CDCl_3$) δ4.69~4.61(m, 1H), 4.57(m, 1H), 3.88~3.79(m, 1H), 3.78~3.69(m, 1H), 1.27~1.17(m, 9H), 1.11(d, *J*=6.3 Hz, 3H), 0.87(s, 9H), 0.06(d, *J*=2.0 Hz, 6H). ^{13}C NMR(125 MHz, $CDCl_3$) δ154.67, 138.54, 128.43, 127.78, 127.70, 79.13, 76.74, 76.21, 71.46, 70.08, 18.95, 16.33, 15.61, 15.34.

Iso-**2**-III的合成: 将*Iso*-**2**-I(25.0 g, 60.9 mmol)溶于250 mL乙腈, 搅拌冷却至0°C后滴加三氟化硼乙醚(46.5wt%, 4.4 mL), 搅拌反应5 min. 加入20 mL饱和碳酸氢钠溶液淬灭反应, 加入50 mL水和200 mL二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得14.4 g *Iso*-**2**-III. 产物为无色油状液体, 产率80%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.39~7.25(m, 5H), 4.91~4.80(m, 1H), 4.68~4.48(m, 3H), 3.81~3.69(m, 1H),

3.65~3.52(m, 1H), 1.26(dd, *J*=9.7, 6.4 Hz, 6H), 1.19(dd, *J*=6.4, 3.8 Hz, 6H). ^{13}C NMR(125 MHz, $CDCl_3$) *δ*154.68, 138.55, 128.45, 127.79, 127.72, 79.16, 76.77, 76.22, 71.48, 70.12, 18.98, 16.37, 15.63, 15.36. HRMS(*m*/*z*): Calcd. for $[C_{16}H_{28}NO_5]^+$: 314.1962, found: 314.1966.

Iso-**2**-IV的合成: 氮气保护下, *Iso*-**2**-III(14.4 g, 48.6 mmol)和无水吡啶(11.8 mL, 145.8 mmol)溶于80 mL无水二氯甲烷, 搅拌冷却至−20°C, 缓慢滴加至三光气(14.4 g, 48.9 mmol)的无水二氯甲烷(200 mL)溶液中, 滴加完毕后升温至0°C, 搅拌反应8 h. 150 mL 1 mol/L盐酸冷却至0°C, 边搅拌边将反应液缓慢倒入盐酸中, 静置分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得15.7 g *Iso*-**2**-IV. 产物为无色油状液体, 产率90%. ^{1}H NMR(400 MHz, $CDCl_3$) *δ*7.39~7.26(m, 5H), 4.99(m, 1H), 4.88(m, 2H), 4.67~4.49(dd, *J*=44.4, 11.8 Hz, 2H), 3.60(m, 1H), 1.37(d, *J*=6.5 Hz, 3H), 1.28(dd, *J*=6.5, 4.1 Hz, 6H), 1.19(d, *J*=6.4 Hz, 3H). ^{13}C NMR(125 MHz, $CDCl_3$) *δ*154.37, 150.32, 138.62, 128.44, 127.72, 127.68, 80.26, 76.22, 74.37, 71.47, 15.95, 15.72, 15.55, 15.33.

Iso-**4**-I的合成: 氮气保护下, *Iso*-**2**-IV(13.3 g, 37.1 mmol)和30 mL无水吡啶溶于100 mL无水四氢呋喃, 得到混合液; *Iso*-**2**-II(11.3 g, 35.4 mmol)溶于50 mL无水四氢呋喃, 滴加至混合液中, 室温搅拌反应6 h. 将反应液倒入250 mL 1 mol/L盐酸中淬灭, 旋去四氢呋喃, 加入二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得10.5 g *Iso*-**4**-I. 产物为无色油状液体, 产率46%. ^{1}H NMR(400 MHz, $CDCl_3$) *δ*7.38~7.27(m, 5H), 4.92~4.78(m, 5H), 4.70~4.48(m, 3H), 3.89~3.78(m, 1H), 3.65~3.54(m, 1H), 1.30~1.24(m, 15H), 1.18(t, *J*=6.4 Hz, 6H), 1.10(d, *J*=6.2 Hz, 3H), 0.87(s, 9H), 0.06(s, 6H). ^{13}C NMR(125 MHz, $CDCl_3$) *δ*154.51, 154.50, 154.31, 138.68, 128.44, 127.73, 127.66, 78.34, 76.68, 76.18, 75.36, 75.05, 74.82, 71.48, 69.61, 25.90, 18.76, 15.79, 15.76, 15.71, 15.43, 15.26, 15.00, −4.53, −4.75. HRMS(*m*/*z*): Calcd. for $[C_{32}H_{58}NO_{11}Si]^+$: 660.3774, found: 660.3784.

Iso-**1**的合成: *Iso*-**4**-I脱除两个保护基(脱除苄基和叔丁基二甲基硅基的方法分别参照*Iso*-**2**-II和*Iso*-**2**-III的合成)后得到中间产物*Iso*-**4**-I′(0.4 g, 0.9 mmol), 在氮气保护下, 溶于15 mL无水二氯甲烷, 加入氯甲酸甲酯(0.9 g, 9.0 mmol), 3.6 mL无水吡啶和4-二甲氨基吡啶(12.2 mg, 0.1 mmol), 0°C搅拌反应12 h. 将反应液倒入50 mL 1 mol/L盐酸中淬灭, 饱和氯化钠溶液洗涤, 所得有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(5:1, 体积比)作洗脱剂柱层析, 得0.4 g *Iso*-**1**. 产物为白色粉末固体, 产率80%. ^{1}H NMR(400 MHz, $CDCl_3$) *δ*4.82(m, 8H), 3.77(s, 6H), 1.45~1.10(m, 24H). ^{13}C NMR(125 MHz, $CDCl_3$) *δ*155.30, 154.24, 154.23, 75.41, 75.35, 75.26, 54.87, 15.80, 15.76. HRMS(*m*/*z*): Calcd. for $[C_{23}H_{42}NO_{15}]^+$: 572.2549, found: 572.2554.

Iso-**4**-III的合成: 将*Iso*-**4**-I(11.2 g, 17.4 mmol)溶于120 mL乙腈, 搅拌冷却至0°C后滴加三氟化硼乙醚(46.5wt%, 2.5 mL), 搅拌反应5 min. 加入20 mL饱和碳酸氢钠溶液淬灭反应, 加入50 mL水和100 mL二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(4:1, 体积比)作洗脱剂柱层析, 获得5.5 g *Iso*-**4**-III. 产物为白色固体粉末, 产率60%. ^{1}H NMR(400 MHz, $CDCl_3$) *δ*7.30(m, 5H), 4.94~4.77(m, 5H), 4.66~4.48(m, 3H), 3.75(m, 1H), 3.59(m, 1H), 1.27(m, 18H), 1.18(dd, *J*=9.0, 6.5 Hz, 6H). ^{13}C NMR(125 MHz, $CDCl_3$) *δ*154.49, 154.31, 138.65, 128.42, 127.71, 127.65, 79.38, 76.69, 76.16, 75.45, 75.39, 75.02, 71.45, 70.03, 18.98, 16.35, 15.87, 15.79, 15.43, 15.25. HRMS(*m*/*z*): Calcd. for $[C_{26}H_{44}NO_{11}]^+$: 546.2909, found: 546.2915.

Iso-**8**-V的合成: 氮气保护下, *Iso*-**4**-III(5.5 g, 10.4 mmol)和无水吡啶(2.1 mL, 31.2 mmol)溶于50 mL无水二氯甲烷, 搅拌冷却至−20°C, 缓慢滴加至三光气(1.1 g, 3.8 mmol)的无水二氯甲烷(50 mL)溶液中, 滴加完毕后升温至0°C, 搅拌反应8 h. 30 mL 1 mol/L盐酸冷却至0°C, 边搅拌边将反应液缓慢倒入盐酸中, 静置分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(3:1, 体积比)作洗脱剂柱层析, 得4.9 g *Iso*-**8**-V. 产物为白色固体粉末, 产率52%. ^{1}H NMR(400 MHz, $CDCl_3$) *δ*7.36~7.23(m, 10H), 4.91~4.76(m, 14H), 4.65~4.48(m, 4H), 3.59(m, 2H), 1.32~1.15(m, 48H). ^{13}C NMR(125 MHz, $CDCl_3$) *δ*154.28, 138.66, 128.44, 127.72, 76.17, 75.35, 75.03, 71.47, 15.80, 15.44, 15.26. HRMS(*m*/*z*): Calcd. for $[C_{53}H_{82}NO_{23}]^+$: 1100.5272, found: 1100.5278.

Iso-**2**的合成: *Iso*-**8**-V脱除两个苄基(脱除苄基的方法参照*Iso*-**2**-II的合成)后得到中间产物*Iso*-**8**-I′(0.5 g, 0.6 mmol), 在氮气保护下, 溶于10 mL无水二氯甲烷, 加

入氯甲酸甲酯(0.5 g, 6.0 mmol), 2.2 mL无水吡啶和4-二甲氨基吡啶(12.2 mg, 0.1 mmol), 0°C 搅拌反应12 h. 将反应液倒入50 mL 1 mol/L盐酸中淬灭, 饱和氯化钠溶液洗涤, 所得有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(4:1, 体积比)作洗脱剂柱层析, 得0.4 g *Iso*-**2**. 产物为白色粉末固体, 产率65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ4.79(m, 16H), 3.74(s, 6H), 1.37~1.12 (m, 48H). ^{13}C NMR(125 MHz, $CDCl_3$) δ155.20, 154.14, 154.12, 75.31, 75.26, 75.24, 75.23, 75.16, 54.79, 30.93, 15.73, 15.71, 15.68. HRMS(*m*/*z*): Calcd. for $[C_{43}H_{74}NO_{17}]^+$: 1036.4443, found: 1036.4448.

(*R*,*R*)-**3**的合成: 氮气保护下, 将(*R*,*R*)-**1**(40.0 g, 443.9 mmol)、溴化苄(151.2 g, 887.8 mmol)、4-氟苯硼酸(6.2 g, 44.4 mmol)、四乙基溴化铵(92.8 g, 443.9 mmol)和氢氧化钾(24.8 g, 443.9 mmol)投入三口烧瓶中, 加入700 mL甲苯, 35°C 搅拌反应36 h. 恢复室温后将反应液倒入300 mL水中, 乙酸乙酯萃取, 振荡后静置分相, 有机相用无水硫酸钠干燥. 减压旋蒸除去溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得42.5 g (*R*,*R*)-**3**. 产物为红棕色油状液体, 产率52%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.42~7.27(m, 5H), 4.56 (dd, *J*=91.1, 11.4 Hz, 2H), 3.69~3.56(m, 1H), 3.32(m, 1H), 1.17(t, *J*=5.7 Hz, 6H). ^{13}C NMR(100 MHz, $CDCl_3$) δ138.44, 128.61, 127.93, 127.89, 80.33, 71.32, 71.16, 18.65, 15.51. HRMS(*m*/*z*): Calcd. for $[C_{11}H_{16}NaO_2]^+$: 203.1043, found: 203.1043.

Syndio-**2**-I的合成: 氮气保护下, (*R*,*R*)-**3**(27.0 g, 149.9 mmol)和60wt%氢化钠(7.2 g, 180.0 mmol)溶于300 mL无水四氢呋喃中, 室温搅拌6 h, 得到混合液. 氮气保护下, (*S*,*S*)-**4**(47.0 g, 157.6 mmol)溶于300 mL无水四氢呋喃中, 将混合液滴入其中, 室温搅拌反应1 h. 将反应液缓慢倾倒入300 mL 1 mol/L盐酸中, pH调为酸性, 减压旋蒸除去四氢呋喃, 加入500 mL二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(15:1, 体积比)作洗脱剂柱层析, 得47.5 g *Syndio*-**2**-I. 产物为无色油状液体, 产率77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.30(m, 5H), 4.91~4.81(m, 1H), 4.71~4.50(m, 3H), 3.91~3.80(m, 1H), 3.66~3.57(m, 1H), 1.27(d, *J*=6.5 Hz, 3H), 1.19(dd, *J*=12.8, 6.4 Hz, 6H), 1.09 (d, *J*=6.3 Hz, 3H), 0.87(s, 9H), 0.06(s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ154.66, 138.70, 128.44, 127.71, 127.65, 77.89, 76.03, 75.80, 71.42, 69.33, 25.97, 25.89, 18.48, 18.12, 15.11, 15.07, 14.70, −4.56, −4.74.

Syndio-**2**-II的合成: 将*Syndio*-**2**-I(18.0 g, 43.8 mmol)和Pd/C(10wt%, 0.9 g)加入高压釜中, 用30 mL乙醇溶解. 高压釜密封好后通入氢气(0.1 MPa), 室温搅拌反应24 h. 过滤除去Pd/C, 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得12.4 g *Syndio*-**2**-II. 产物为无色油状液体, 产率88%. ^{1}H NMR(400 MHz, $CDCl_3$) δ4.68~4.60(m, 1H), 4.57(m, 1H), 3.90~3.81(m, 1H), 3.75(m, 1H), 1.27(d, *J*=6.4 Hz, 3H), 1.19(t, *J*= 6.7 Hz, 6H), 1.10(d, *J*=6.3 Hz, 3H), 0.86(s, 9H), 0.06(s, 6H). ^{13}C NMR(125 MHz, $CDCl_3$) δ154.65, 78.92, 78.25, 69.99, 69.45, 25.85, 18.88, 18.68, 18.11, 16.24, 14.91, −4.55, −4.74.

Syndio-**2**-III的合成: 将*Syndio*-**2**-I(22.0 g, 53.8 mmol)溶于200 mL乙腈, 搅拌冷却至0°C 后滴加三氟化硼乙醚(46.5wt%, 4.0 mL), 搅拌反应5 min. 加入20 mL饱和碳酸氢钠溶液淬灭反应, 加入50 mL水和200 mL二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得14.5 g *Syndio*-**2**-III. 产物为无色油状液体, 产率91%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.30(m, 5H), 4.92~4.81(m, 1H), 4.68~4.48(m, 3H), 3.74(m, 1H), 3.61 (m, 1H), 1.27(dd, *J*=6.5, 2.0 Hz, 6H), 1.17(t, *J*= 6.6 Hz, 6H). HRMS(*m*/*z*): Calcd. for $[C_{16}H_{28}NO_5]^+$: 314.1962, found: 314.1960.

Syndio-**2**-IV的合成: 氮气保护下, *Syndio*-**2**-III (14.5 g, 48.9 mmol)和无水吡啶(11.8 mL, 145.8 mmol)溶于80 mL无水二氯甲烷, 搅拌冷却至−20°C, 缓慢滴加至三光气(14.4 g, 48.9 mmol)的无水二氯甲烷(200 mL)溶液中, 滴加完毕后升温至0°C, 搅拌反应8 h. 150 mL 1 mol/L盐酸冷却至0°C, 边搅拌边将反应液缓慢倒入盐酸中, 静置分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(10:1, 体积比)作洗脱剂柱层析, 得12.8 g *Syndio*-**2**-IV. 产物为无色油状液体, 产率73%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.31(m, 5H), 5.00(m, 1H), 4.95~4.80(m, 6H), 4.67~4.51(m, 2H), 3.62 (m, 1H), 1.38(d, *J*=6.5 Hz, 3H), 1.30(m, 18H), 1.18(d, *J*= 6.4 Hz, 3H). ^{13}C NMR(125 MHz, $CDCl_3$) δ154.30, 150.31, 138.58, 128.45, 127.71, 127.68, 80.16, 77.09, 75.88, 74.43, 71.46, 16.00, 15.66, 15.43, 15.20.

Syndio-**4**-I的合成: 氮气保护下, *Syndio*-**2**-IV(12.7 g, 35.4 mmol)和30 mL无水吡啶溶于100 mL无水四氢呋

喃, 得到混合液; *Syndio*-2-II(10.8 g, 33.7 mmol)溶于50 mL无水四氢呋喃, 滴加至混合液中, 室温搅拌反应6 h. 将反应液倒入200 mL 1 mol/L盐酸中淬灭, 旋去四氢呋喃, 加入二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(15:1, 体积比)作洗脱剂柱层析, 得19.2 g *Syndio*-4-I. 产物为白色固体粉末, 产率89%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.39~7.26(m, 5H), 4.91~4.76(m, 5H), 4.69~4.49(m, 3H), 3.91~3.81(m, 1H), 3.66~3.55(m, 1H), 1.27(dd, J= 9.4, 6.5 Hz, 15H), 1.18(dd, J=13.8, 6.4 Hz, 6H), 1.10(d, J=6.3 Hz, 3H), 0.87(s, 9H), 0.06(s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ154.44, 154.38, 154.24, 138.64, 128.44, 127.71, 127.65, 78.19, 76.62, 75.89, 75.21, 75.12, 74.85, 74.70, 71.45, 69.24, 25.88, 18.46, 18.11, 15.69, 15.64, 15.56, 15.52, 15.26, 15.12, 14.65, −4.57, −4.73.

Syndio-**1**的合成: *Syndio*-**4**-I脱除两个保护基(脱除苄基和叔丁基二甲基硅基的方法分别参照*Syndio*-**2**-II和*Syndio*-**2**-III的合成)后得到中间产物*Syndio*-**4**-I′(1.2 g, 2.7 mmol), 在氮气保护下, 溶于5 mL无水二氯甲烷, 加入氯甲酸甲酯(2.5 g, 27.0 mmol), 2 mL无水吡啶和4-二甲氨基吡啶(12.2 mg, 0.1 mmol), 0°C 搅拌反应12 h. 将反应液倒入50 mL 1 mol/L盐酸中淬灭, 饱和氯化钠溶液洗涤, 所得有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(5:1, 体积比)作洗脱剂柱层析, 得1.1 g *Syndio*-**1**. 产物为白色粉末固体, 产率72%. ^{1}H NMR(400 MHz, $CDCl_3$) δ5.06~4.57(m, 8H), 3.75(s, 6H), 1.27(d, J=5.6 Hz, 24H). ^{13}C NMR(100 MHz, $CDCl_3$) δ155.30, 154.20, 154.18, 75.34, 75.29, 75.18, 75.15, 54.86, 15.77, 15.64, 15.59. HRMS(m/z): Calcd. for $[C_{23}H_{38}NaO_{15}]^{+}$: 577.2103, found: 577.2086.

Syndio-**4**-II的合成: 将*Syndio*-**4**-I(1.9 g, 3.0 mmol)和Pd/C(10wt%, 0.1 g)加入高压釜中, 用5 mL乙醇溶解. 高压釜密封好后通入氢气(0.1 MPa), 室温搅拌反应24 h. 过滤除去Pd/C, 旋干溶剂, 粗产物用石油醚/丙酮(6:1, 体积比)作洗脱剂柱层析, 得1.1 g *Syndio*-**2**-II. 产物为白色固体粉末, 产率66%. ^{1}H NMR(400 MHz, $CDCl_3$) δ4.83(m, 4H), 4.61(m, 2H), 3.86(m, 1H), 3.75(m, 1H), 1.35~1.25(m, 15H), 1.19(t, J=5.8 Hz, 6H), 1.10(d, J=6.2 Hz, 3H), 0.87(s, 9H), 0.06(s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ154.50, 154.40, 154.25, 79.29, 78.25, 75.46, 75.28, 75.19, 74.80, 69.95, 69.24, 25.88, 19.01, 18.47, 18.12, 16.30, 15.94, 15.55, 14.65, −4.56, −4.73. HRMS(m/z): Calcd. for $[C_{25}H_{48}NaO_{11}Si]^{+}$: 575.2858, found: 575.2859.

Syndio-**4**-III的合成: 将*Syndio*-**4**-I(12.0 g, 18.7 mmol)溶于120 mL 乙腈, 搅拌冷却至0°C后滴加三氟化硼乙醚(46.5wt%, 2.6 mL), 搅拌反应5 min. 加入20 mL 饱和碳酸氢钠溶液淬灭反应, 加入50 mL水和100 mL二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(4:1, 体积比)作洗脱剂柱层析, 得9.2 g *Syndio*-**4**-III. 产物为白色固体粉末, 产率93%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.29(m, 5H), 4.82(m, 5H), 4.66~4.46(m, 3H), 3.74(m, 1H), 3.60(m, 1H), 1.35~1.20(m, 18H), 1.17(t, J=5.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ154.46, 154.40, 154.22, 138.59, 128.41, 127.70, 127.62, 79.20, 76.71, 75.83, 75.49, 75.29, 75.24, 75.06, 71.42, 69.82, 18.92, 16.24, 15.92, 15.73, 15.68, 15.27, 15.13. HRMS(m/z): Calcd. for $[C_{26}H_{44}NO_{11}]^{+}$: 546.2909, found: 546.2911.

Syndio-**4**-IV的合成: 氮气保护下, *Syndio*-**4**-III (3.0 g, 5.7 mmol)和无水吡啶(1.4 mL, 17.0 mmol)溶于15 mL无水二氯甲烷, 搅拌冷却至−20°C, 缓慢滴加至三光气(1.7 g, 5.7 mmol)的无水二氯甲烷(10 mL)溶液中, 滴加完毕后升温至0°C, 搅拌反应8 h. 50 mL 1 mol/L盐酸冷却至0°C, 边搅拌边将反应液缓慢倒入盐酸中, 静置分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(5:1, 体积比)作洗脱剂柱层析, 得2.8 g *Syndio*-**4**-IV. 产物为白色固体粉末, 产率83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.31(m, 5H), 5.00(m, 1H), 4.95~4.80 (m, 6H), 4.67~4.51(m, 2H), 3.62(m, 1H), 1.38(d, J= 6.5 Hz, 3H), 1.30(m, 18H), 1.18(d, J=6.4 Hz, 3H). ^{13}C NMR(100 MHz, $CDCl_3$) δ154.35, 154.16, 154.02, 150.20, 138.55, 128.37, 127.63, 127.58, 80.01, 76.57, 75.82, 75.48, 75.23, 75.05, 74.79, 74.66, 71.35, 15.90, 15.65, 15.58, 15.23, 15.06. HRMS (m/z): Calcd. for $[C_{27}H_{43}ClNO_{12}]^{+}$: 608.2468, found: 608.2469.

Syndio-**8**-I的合成: 氮气保护下, *Syndio*-**4**-IV(2.0 g, 3.4 mmol)和5 mL无水吡啶溶于15 mL无水四氢呋喃, 得到混合液; *Syndio*-**4**-II(1.8 g, 3.3 mmol)溶于10 mL无水四氢呋喃, 滴加至混合液中, 室温搅拌反应6 h. 将反应液倒入80 mL 1 mol/L盐酸中淬灭, 旋去四氢呋喃, 加入二氯甲烷萃取分相, 有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(5:1, 体积比)作洗脱剂柱层

析, 得3.4 g *Syndio*-**8**-I. 产物为白色固体粉末, 产率93%. ^{1}H NMR(400 MHz, $CDCl_3$) δ7.28(m, 5H), 4.93~4.71(m, 15H), 4.67~4.46(m, 3H), 3.84(m, 1H), 3.58(m, 1H), 1.25 (t, *J*=7.9 Hz, 39H), 1.16(dd, *J*=14.2, 6.4 Hz, 6H), 1.08(d, *J*=6.3 Hz, 3H), 0.85(s, 9H), 0.04(s, 6H).

Syndio-**2**的合成: *Syndio*-**8**-I脱除两个保护基(脱除苄基和叔丁基二甲基硅基的方法分别参照*Syndio*-**2**-II和*Syndio*-**2**-III的合成)后得到中间产物*Syndio*-**8**-I′(0.6 g, 0.7 mmol), 在氮气保护下, 溶于10 mL无水二氯甲烷, 加入氯甲酸甲酯(0.6 g, 7.0 mmol), 3 mL无水吡啶和4-二甲氨基吡啶(12.2 mg, 0.1 mmol), 0°C 搅拌反应12 h. 将反应液倒入50 mL 1 mol/L盐酸中淬灭, 饱和氯化钠溶液洗涤, 所得有机相用无水硫酸钠干燥. 旋干溶剂, 粗产物用石油醚/丙酮(5:1, 体积比)作洗脱剂柱层析, 得0.3 g *Syndio*-**2**. 产物为白色粉末固体, 产率45%. ^{1}H NMR(400 MHz, $CDCl_3$) δ4.97~4.69(m, 16H), 3.77(s, 6H), 1.28(d, *J*=6.2 Hz, 48H). ^{13}C NMR(100 MHz, $CDCl_3$) δ155.20, 154.10, 154.07, 75.24, 75.19, 75.05, 75.03, 54.77, 15.67, 15.54, 15.49. HRMS(*m*/*z*): Calcd. for $[C_{43}H_{74}NO_{17}]^+$: 1036.4443, found: 1036.4441.

2 结果与讨论

聚碳酸-2,3-丁烯酯(poly(2,3-butene carbonate), PBC)的全同四聚寡聚物*Iso*-**1**合成策略如图3所示. 以对映体过量(*ee*)>98%的(*S*,*S*)-**1**为起始原料, 将其分为两部分, 分别对其羟基进行苄基(Bn)和叔丁基二甲基硅基(TBS)单保护, 得到(*S*,*S*)-**3**和(*S*,*S*)-**2**. 其中, (*S*,*S*)-**2**与*N*,*N*′-羰基二咪唑反应获得(*S*,*S*)-**4**, 再与(*S*,*S*)-**3**进行缩合, 得到二聚体*Iso*-**2**-I. 将*Iso*-**2**-I分为两部分, 分别脱去Bn和TBS, 得到*Iso*-**2**-II和*Iso*-**2**-III. 其中, *Iso*-**2**-III和三光气反应制备*Iso*-**2**-IV, 其再与*Iso*-**2**-II进行缩合, 得到全同四聚体*Iso*-**4**-I. 应当强调的是, 若此处使用*N*,*N*′-羰基二咪唑作为缩合的中间试剂, 在氢化钠的强碱性条件下, *Iso*-**2**-II非常容易发生回咬, 降解为(*S*,*S*)-**2**和环状碳酸酯(图4). 而采用三光气, 缩合反应只需在吡啶的弱碱性条件下即可进行, 避免了降解副反应的发生, 这一合成方法较Nozaki课题组[38]的逐步合成法有了极大的改进, 这也为我们以后合成更长单元数的寡聚物提供可能. 最后, 将*Iso*-**4**-I脱去Bn和TBS, 再用氯甲酸甲酯进行封端, 即可得到与聚合物结构相似的模型全同四聚体*Iso*-**1**. 全同八聚体*Iso*-**2**的合成方法与*Iso*-**1**略有不同, *Iso*-**4**-I脱去TBS得到*Iso*-**4**-III, 再与不足量的三光气反应, 可一步生成端基均为Bn的八聚体*Iso*-**8**-V. *Iso*-**8**-V脱去Bn后用氯甲酸甲酯封端, 最终得到与聚合物结构相似的模型全同八聚体*Iso*-**2**.

PBC的间同四聚寡聚物*Syndio*-**1**的合成策略与*Iso*-**1**相同, 但间同八聚寡聚物*Syndio*-**2**的合成与*Iso*-**2**有所不同, 如图5所示. 为了确保间同度, 需要将*Syndio*-**4**-I

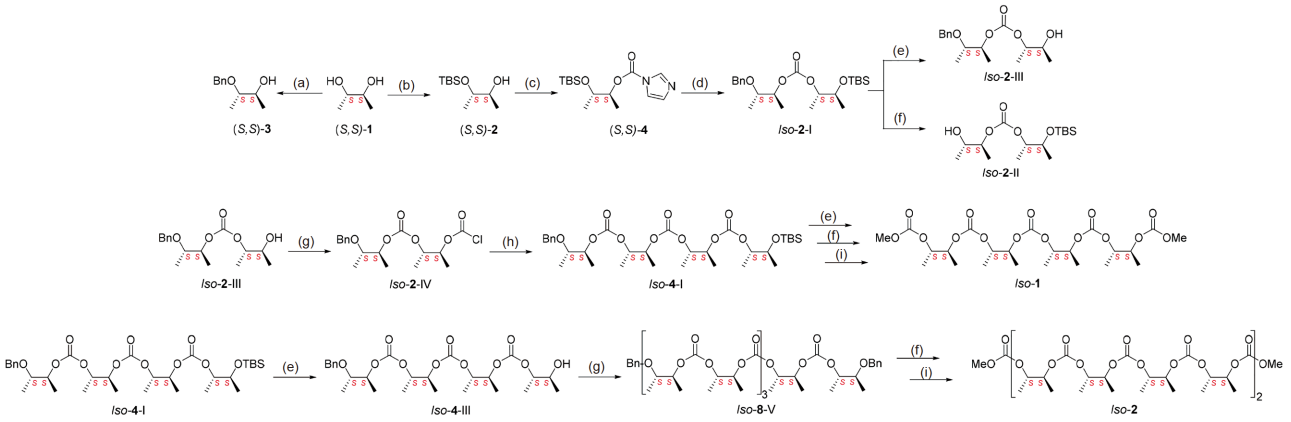

图 3 (网络版彩色)全同结构聚碳酸-2,3-丁烯酯寡聚物*Iso*-**1**(四聚体)和*Iso*-**2**(八聚体)的合成路线. (a) 溴化苄、4-氟苯硼酸、四乙基溴化铵、氢氧化钾、甲苯、35°C; (b) 叔丁基二甲硅基三氟甲磺酸酯、三乙胺、二氯甲烷、0°C至室温; (c) *N*,*N*′-羰基二咪唑、1,8-二氮杂二环十一碳-7-烯、四氢呋喃、室温; (d) (*S*,*S*)-**3**、氢化钠、四氢呋喃、室温; (e) 三氟化硼乙醚、乙腈、0°C; (f) 氢气、钯碳催化剂、乙醇、室温; (g) 三光气、吡啶、二氯甲烷、−20~0°C; (h) *Iso*-**2**-II、吡啶、四氢呋喃、25°C; (i) 氯甲酸甲酯、吡啶、4-二甲氨基吡啶、二氯甲烷、0°C

Figure 3 (Color online) Synthetic route of isotactic poly(2,3-butene carbonate) oligomers *Iso*-**1** (tetramer) and *Iso*-**2** (octamer). (a) BnBr, *p*-FPhB$(OH)_2$, Et_4NBr, KOH, toluene, 35°C; (b) TBSOTf, Et_3N, CH_2Cl_2, 0°C to room temperature (r.t.); (c) Im_2CO, DBU, THF, r.t.; (d) (*S*,*S*)-**3**, NaH, THF, r.t.; (e) $BF_3{\cdot}Et_2O$, CH_3CN, 0°C; (f) H_2, Pd/C, EtOH, r.t.; (g) triphosgene, pyridine, CH_2Cl_2, −20 to 0°C; (h) *Iso*-**2**-II, Pyridine, THF, 25°C; (i) $ClCO_2Me$, pyridine, DMAP, CH_2Cl_2, 0°C

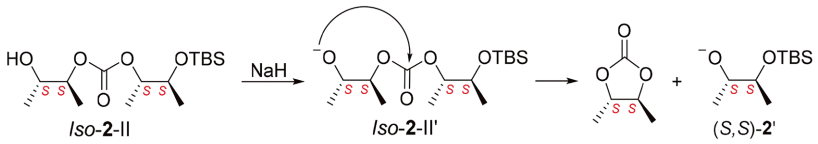

图 4 (网络版彩色)*Iso*-**2**-II的降解
Figure 4 (Color online) Degradation of *Iso*-**2**-II

分为两部分, 分别脱去Bn和TBS, 得到*Syndio*-**4**-II和*Syndio*-**4**-III. 其中, *Syndio*-**4**-III和三光气反应形成*Syndio*-**4**-IV, 然后再与*Syndio*-**4**-II缩合, 得到八聚体*Syndio*-**8**-I. 最后, 将*Iso*-**8**-I脱去Bn和TBS, 再用氯甲酸甲酯进行封端, 即可得间同八聚体*Syndio*-**2**.

图6是全同和间同结构碳酸-2,3-丁烯酯四聚体(*Iso*-**1**和*Syndio*-**1**)和八聚体(*Iso*-**2**和*Syndio*-**2**), 以及无规PBC和全同PBC的核磁碳谱. 如图所示, *Iso*-**1**和*Iso*-**2**的中心羰基碳化学位移均为154.12 ppm, 与全同PBC的羰基碳(154.12 ppm)相同; 次甲基碳分别在75.24和75.23 ppm处出峰, 与聚合物的次甲基碳出峰位置(75.22 ppm)基本对应; 侧链上甲基碳的化学位移分别为15.69和15.71 ppm, 与聚合物的甲基碳(15.72 ppm)亦基本匹配. 对比*Iso*-**1**和*Iso*-**2**, 随着寡聚物单元数的增加, 中心羰基碳、次甲基碳和侧链甲基碳的化学位移逐渐向聚合物靠近, 其端位基团的影响变小. *Syndio*-**1**和*Syndio*-**2**的中心羰基碳分别在154.10和154.09 ppm处出峰, 比*Iso*-**1**和*Iso*-**2**低0.02~0.03 ppm; 次甲基碳的信号(分别为75.09和75.07 ppm)与全同聚合物的偏差更明显; 从甲基碳区域可以更清晰地观察到, 聚合物的间同单元序列的甲基碳在15.51 ppm处出峰. 此外, 155.20和54.78 ppm附近的信号分别对应寡聚物端基的羰基碳和甲基碳.

3 结论

本研究以手性2,3-丁二醇为起始原料, 合成了聚碳酸-2,3-丁烯酯的全同结构四聚体*Iso*-**1**和八聚体*Iso*-**2**, 间同结构四聚体*Syndio*-**1**和八聚体*Syndio*-**2**. 使用固体

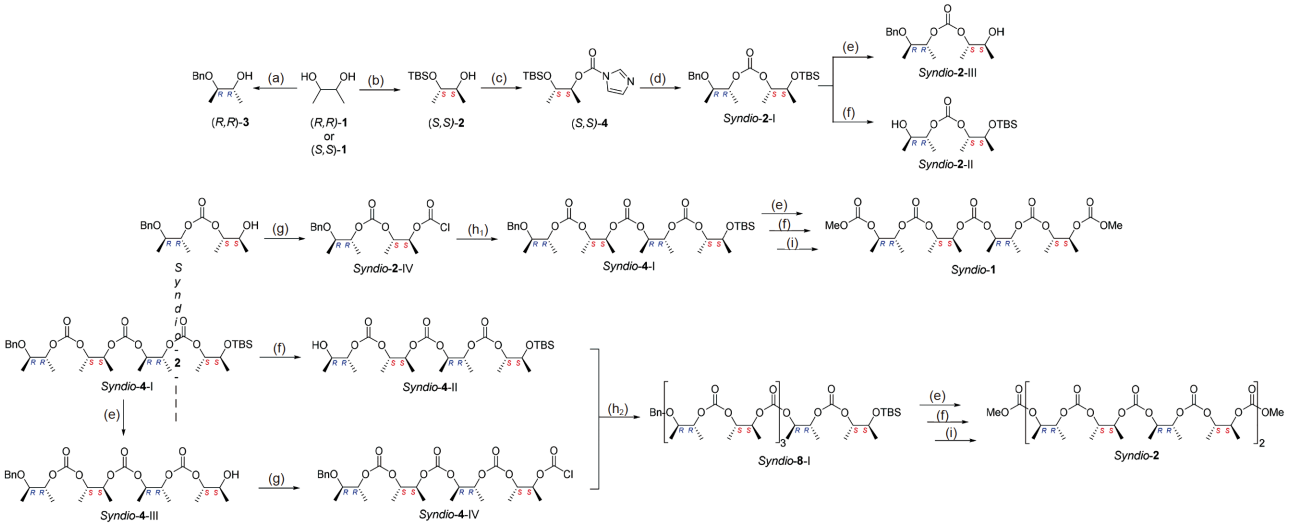

图 5 (网络版彩色)间同结构聚碳酸-2,3-丁烯酯寡聚物*Syndio*-**1**(四聚体)和*Syndio*-**2**(八聚体)的合成路线. (a) 溴化苄、4-氟苯硼酸、四乙基溴化铵、氢氧化钾、甲苯, 35°C; (b) 叔丁基二甲基三氟甲磺酸酯、三乙胺、二氯甲烷、0°C至室温; (c) *N*,*N*′-羰基二咪唑、1,8-二氮杂二环十一碳-7-烯、四氢呋喃、室温; (d) (*R*,*R*)-**3**、氢化钠、四氢呋喃、室温; (e) 三氟化硼乙醚、乙腈、0°C; (f) 氢气、钯碳催化剂、乙醇、室温; (g) 三光气、吡啶、二氯甲烷、−20~0°C; (h_1) *Syndio*-**2**-II、吡啶、四氢呋喃、25°C; (h_2) 吡啶、四氢呋喃、25°C; (i) 氯甲酸甲酯、吡啶、4-二甲氨基吡啶、二氯甲烷、0°C
Figure 5 (Color online) Synthetic route of syndiotactic poly(2,3-butene carbonate) oligomers *Syndio*-**1** (tetramer) and *Syndio*-**2** (octamer). (a) BnBr, *p*-FPhB(OH)$_2$, Et_4NBr, KOH, toluene, 35°C; (b) TBSOTf, Et_3N, CH_2Cl_2, 0°C to r.t.; (c) Im_2CO, DBU, THF, r.t.; (d) (*R*,*R*)-**3**, NaH, THF, r.t.; (e) $BF_3{\cdot}Et_2O$, CH_3CN, 0°C; (f) H_2, Pd/C, EtOH, r.t.; (g) triphosgene, pyridine, CH_2Cl_2, −20 to 0°C; (h_1) *Syndio*-**2**-II, pyridine, THF, 25°C; (h_2) pyridine, THF, 25°C; (i) $ClCO_2Me$, pyridine, DMAP, CH_2Cl_2, 0°C

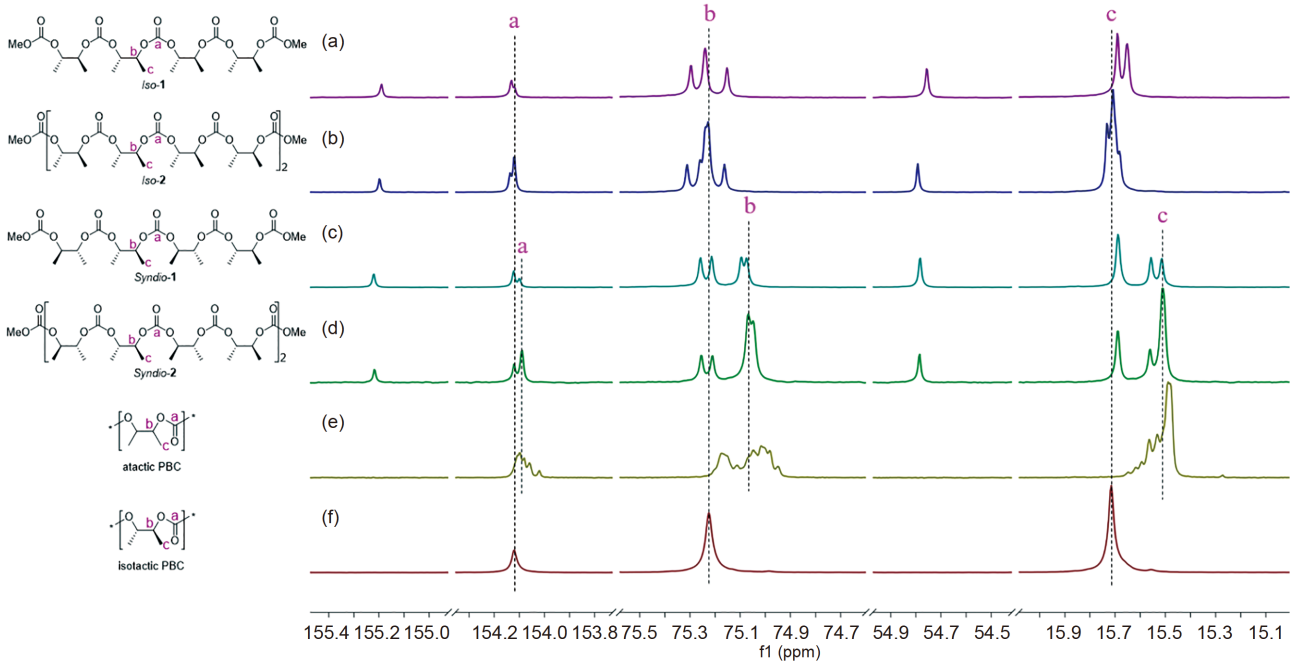

图 6 (网络版彩色)*Iso*-**1**(a), *Iso*-**2**(b), *Syndio*-**1**(c), *Syndio*-**2**(d), 无规PBC(*ee*=0)(e)和全同PBC(*ee*>99%)(f)的核磁碳谱. (a)~(c)分别归属羰基、次甲基和甲基碳原子的化学位移

Figure 6 (Color online) Carbonyl (a), methine (b) and methyl (c) regions of ^{13}C NMR spectra of *Iso*-**1** (a), *Iso*-**2** (b), *Syndio*-**1** (c), *Syndio*-**2** (d), atactic PBC with *ee*=0 (e) and isotactic PBC with >99% *ee* (f)

三光气代替常用*N*,*N*′-羰基二咪唑羰化试剂是成功合成更长单元数立体寡聚物的关键, 使缩合反应只需在吡啶的弱碱性条件下进行, 避免了降解副反应的发生. 通过对所合成聚碳酸-2,3-丁烯酯立体寡聚物的核磁碳谱分析, 羰基碳、次甲基碳和侧链甲基碳在154.12、75.23和15.71化学位移处的信号对应该聚碳酸酯的全同单元序列; 154.09、75.07和15.51处的信号对应聚合物的间同单元序列.

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Summary for "CO_2/顺式-2,3-环氧丁烷交替共聚物的立体寡聚物合成及微结构分析"

Synthesis and microstructure analysis of stereoregular oligomers of CO_2/*cis*-2,3-butene oxide alternating copolymer

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The utilization of carbon dioxide (CO_2) as a nontoxic, abundant, economical and renewable C1 building block for the production of valuable organic chemicals can contribute to a more sustainable chemical industry. In the chemical process using CO_2 as a raw material, the synthesis of degradable aliphatic polycarbonates by alternating copolymerization with epoxides has attracted widespread attention. Notably, aliphatic polycarbonates with biocompatibility and biodegradability have gradually attracted great attention in the field of biomedicine in recent decades, since Inoue and co-workers first reported the copolymerization of CO_2 and epoxides to produce biodegradable CO_2-based polycarbonates by using heterogeneous catalyst in 1969. This method used non-toxic and inexpensive CO_2 to replace the highly toxic phosgene in the traditional polycondensation as carbonylation reagent. Since then, many heterogeneous and homogeneous catalysts systems have been developed for this copolymerization. However, the commercial applications of aliphatic polycarbonates have very limited due to their poor thermal stability and the mechanical properties in comparison with polyolefins. Recently, the binary or bifunctional catalyst based on metal-salen complexes was found to be very efficient for this transformation in immortal polymerization mode, affording various polycarbonates with complete alternating nature, and excellent region- and stereo-selectivity. Along with the discovery of these highly stereoregular catalyst systems that can generate copolymers with high stereoregularity, study on the regiochemistry of epoxides ring-opening during the copolymerization and the stereochemistry of the carbonate unit sequence in the polymer main chain was also reported. The stereochemistry of a polymer significantly affects its physical property. For biodegradable polymers, e.g., polylactide, the degradation rate of isotactic polymers is much slower than that of amorphous polymers due to the orderly arrangement of building units in the former. Additionally, the relative stereochemistry in a polymeric chain also bears a memory of the reaction pathway leading to its formation. Therefore, the assignment of the stereochemistry information on a polymer chain is beneficial for understanding the polymerization mechanism and further designing more efficient catalyst systems. The microstructure information of a polymer can be obtained by analyzing its NMR spectrum. However, since the difference in chemical shifts of the same atom in different stereochemical environments is very small, it is quite difficult to assign the nuclear magnetic signals of polycarbonates. The signals of carbonyl and methine regions in the main chain in the ^{13}C NMR spectra are significantly affected by stereochemistry of polycarbonates. As a consequence, the chemical shift and split of carbonyl and methane in the ^{13}C NMR spectra are used to characterize the microstructure of polycarbonates. The accurate microstructure analysis of a polymer is performed by synthesizing the corresponding model oligomers and analysis of their ^{13}C NMR spectra. In the present contribution, four kinds of model compounds of poly(2,3-butene carbonate): isotactic and syndiotactic tetramers and octamers, were synthesized by the use of chiral 2,3-butanediols as starting materials and triphosgene as carbonylation reagent, which not only avoided the degradation to cyclic carbonate during synthesis but also ensured a fast and reliable increase in the number of oligomer units. By comparing the signals in the ^{13}C NMR spectra of steroregular oligomers, it could be concluded that the signals at 154.12, 75.23 and 15.71 ppm were attributed to carbonyl, methine and methyl of isotactic polymer, respectivey, while the signals at 154.09, 75.07 and 15.51 ppm were assigned to carbonyl, methine and methyl of syndiotactic polymer, respectively.

CO_2, polycarbonate, oligomer, microstructure, NMR spectroscopy

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