Polymer Assembly

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Crystalline Hetero-Stereocomplexed Polycarbonates Produced from Amorphous Opposite Enantiomers Having Different Chemical Structures**

*Ye Liu, Meng Wang, Wei-Min Ren, Yue-Chao Xu, and Xiao-Bing Lu**

Abstract: *Stereocomplexation is the stereoselective interaction between two opposite enantiomeric polymers through an interlocked orderly assembly. Most studies focus on the stereocomplex formation from the crystalline opposite enantiomers having the identical structure; nevertheless, rare examples were reported regarding the crystalline stereocomplexes from enantiomeric polymers having different chemical structures. Herein we show a strategy for polymer orderly assembly through the formation of crystalline hetero-stereocomplexed polymeric materials by the cocrystallization of amorphous isotactic polycarbonates with different chemical structures and opposite configurations. The behaviors in the crystalline state are significantly different from that of the component enantiomeric polymers or their homo-stereocomplexes. This study is expected to open up a new way to prepare various semicrystalline materials having a wide variety of physical properties and degradability.*

Molecular interactions (noncovalent forces) are essential for biological systems such as the self-assembly of protein complexes, selective recognition of enzymes, and the intermolecular reading of genetic code.[1] Under certain conditions, they drive the spontaneous association of molecules into stable and well-defined aggregates with specific functions by selectively binding substrate species. Polymer stereocomplexation is the stereoselective interaction between two opposite enantiomers through an interlocked orderly assembly. In comparison with the parent polymers, stereocomplexes usually show improved thermal and mechanical properties.[2] The representative example is the most widely studied polylactide. Enantiopure semicrystalline (D)- and (L)-polylactides with isotactic configurations are mixed in equivalent amounts to form a novel stereocomplex with an enhanced melting temperature (T_m) of 230 °C, which is about 50 °C higher than that of the individual homopolymers.[3] The better mechanical and thermal properties associated with the polylactide stereocomplex might be able to extend the range of its application in the medical field.[4] Also, because of its more compact crystalline structure, the stereocomplexed polylactide shows a slower degradation rate compared to the component enantiomers. Similarly, in comparison to the enantiopure parent polymers, a significant improvement in thermal properties (both T_m and crystallinity) was also observed in the poly(propylene succinate) stereocomplex, a new class of semicrystalline biodegradable polyesters.[5]

CO_2-based polycarbonates are also novel biodegradable polymers with many potential applications,[6] though these copolymers from terminal epoxides usually suffer from poor thermal resistance due to their lower glass transition temperature (T_g) compared to the widely used bisphenol A polycarbonate (BPA-PC), a plastic prepared from the interfacial polycondensation of bisphenol A with toxic phosgene or through melt transesterification with diphenyl carbonate.[7] BPA-PC has a high T_g up to 150 °C, possessing wonderful thermal deformation resistance, optical clarity, and moldability. Crystalline forms of the polymer have T_ms of 220–260 °C. Unfortunately, though BPA-PC production is still increasing at a rate of three million pounds per year, arguments and disputes on this material have never stopped since its industrialization as early as the 1960s.[8] These controversies are not only focused on its industrialization technologies which caused serious pollution of the environment, but also concerned with the potential health risks exposure to bisphenol A leaching out from BPA-based products.[9] Some studies have linked bisphenol A to reproductive abnormalities and a heightened risk of breast and prostate cancers, diabetes, and heart disease.[10] This has prompted many countries to set laws and regulations that forbid the use of BPA-based polymers in the foodstuff and beverage industry, particularly with regard to baby bottles.[11] Therefore, the development of more environmentally benign routes to producing polycarbonates with excellent properties comparable to that of the traditional BPA-PC is highly desirable.

The pioneer study came with the use of Co^{III} complexes for the copolymerization of CO_2 with indene oxide to afford the corresponding polycarbonate with a T_g up to 138 °C, the highest record for CO_2-based polycarbonates.[12] Nevertheless, the resultant polymer is typically amorphous due to the lack of stereoregularity. In recent contributions, we prepared a series of highly enantiopure polycarbonates by the desymmetrization copolymerization of CO_2 with various *meso*-epoxides.[13,14] Some of them are typical semicrystalline polymers, possessing T_ms of 180–275 °C, dependent on the structure of the employed *meso*-epoxides.[14] Prior to this

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[*] Dr. Y. Liu, M. Wang, W.-M. Ren, Y.-C. Xu, Prof. Dr. X.-B. Lu
State Key Laboratory of Fine Chemicals
Dalian University of Technology
Dalian 116024 (China)
E-mail: xblu@dlut.edu.cn

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discovery, Coates and co-workers have reported that the dinuclear Co^{III} complexes with a binaphthol linker were highly active and enantioselective for homopolymerization of monosubstituted epoxides.[15] Notably, an enhanced T_m and different crystalline behavior was observed in the 1:1 mixture of (*R*)- and (*S*)-poly(cyclohexene carbonate) (PCHC), suggesting the formation of a stereocomplexed polycarbonate.[16] More recently, Coates et al.[17] and our group[18] independently disclosed the formation of crystalline stereocomplexes from the cocrystallization of amorphous enantiomeric polymers. Prior to these studies, Nozaki and co-workers disclosed a novel stereogradient poly(propylene carbonate)s (PPCs) consisting of two enantiomeric structures on each end, which possesses a higher thermal decomposition temperature than the typical PPCs.[19] This was ascribed to the formation of a stereocomplex between two enantiopure components of the polymeric main chains.

Herein, we report the selective synthesis of highly isotactic polycarbonates possessing comparable thermal stability with BPA-PC through stereospecific copolymerization of CO_2 with six-membered *meso*-epoxides: 1,4-dihydronaphthalene oxide (CDO), and 1,2-epoxy-4-cyclohexene (CEO; Figure 1). Further exploration of the stereocomplexation of these stereoregular polycarbonates led to the discovery of various novel crystalline homo- and hetero-stereocomplexed polycarbonates formed by cocrystallization of amorphous opposite enantiomers (Figure 2).

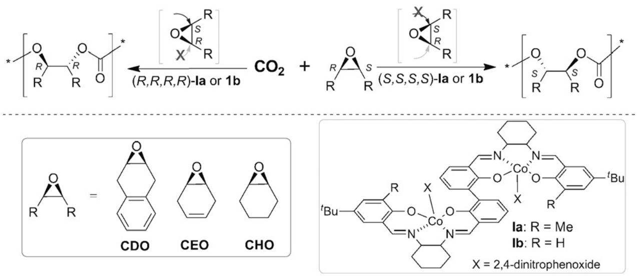

Figure 1. Dinuclear Co^{III}-complex-mediated copolymerization of *meso*-epoxides with CO_2.

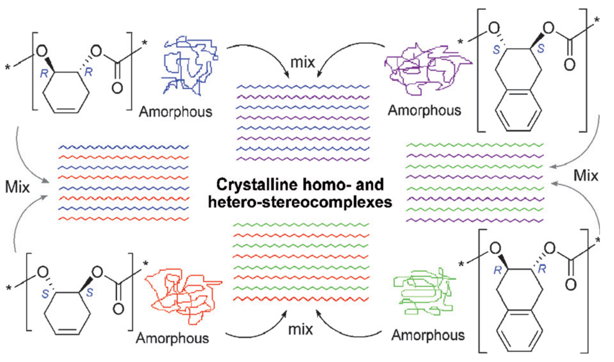

Figure 2. Orderly assembly of various polymers: synthesis of homo- and hetero-stereocomplexed polycarbonates from opposite enantiomers.

In previous contributions, we have demonstrated that the enantiopure biphenol-linked dinuclear Co^{III} complexes **Ia** and **Ib** (Figure 1) are privileged chiral catalysts for the desymmetrization copolymerization of CO_2 with *meso*-epoxides, affording the corresponding polycarbonates with perfectly alternating mode and excellent enantioselectivity.[13b,14,20] As anticipative, these dinuclear Co^{III} complexes were also shown to be very efficient in copolymerizing CO_2 with the six-membered *meso*-epoxides CEO or CDO to give the polycarbonates with $>99\%$ carbonate unit content and 99% enantioselectivity under mild conditions (Supporting Information, SI, Table S1). On the basis of ^1H NMR analysis, neither cyclic carbonates nor a polyether structure was detected in the reaction mixture (Figure S3). A MALDI-TOF study further indicates that the resultant copolymers have perfectly alternating nature (Figures S4 and S5). It is worthwhile noting here parenthetically that prior to our study, Darensbourg and co-workers had reported the salenCr^{III}Cl/*N*-methylimidazole catalyzed coupling reaction of CO_2 and CDO, which predominantly affords the *cis* cyclic carbonate product.[21]

Although the accurate assignment of the microstructures of CO_2/CEO copolymer (PCEC) and poly(1,4-dihydronaphthalene carbonate) (PCDC) proved to be very difficult due to the lack of information regarding their oligomers with various configurations, a ^{13}C NMR study could clearly reveal significant differences in the carbonyl, methine, and methylene regions between the atactic and highly isotactic copolymers (Figure S7). Moreover, it was demonstrated that the *ee* value of diols from the hydrolysis of isotactic polycarbonates was up to 99% based on chiral GC analysis (Figures S8–11).

Differential scanning calorimetry (DSC) was used to determine the thermal properties of the resultant enantiopure polycarbonates. Surprisingly, the DSC thermograms of both highly isotactic PCEC and PCDC with 99% *ee* show no crystallinity (Figure 3, top, plots A and B). Wide-angle X-ray diffraction (WAXD) analysis also confirmed the results (Figure 3, bottom, plots A and B). This is in marked contrast with the isotactic PCHC from cyclohexene oxide, which was demonstrated to be a typical semicrystalline polymer.[13a] It has to be emphasized that isotactic PCDC possesses a high T_g of 150 °C, which is very close to the BPA-based polycarbonates (Figure 3, top, plot A). The isotactic PCEC also has a high T_g of 130 °C (Figure 3, top, plot B).[22]

To test the interaction of opposite configuration polymers, a 1:1 mixture of (*R*)-PCDC ($M_n = 24.7\ \mathrm{kg\,mol^{-1}}$, PDI = 1.18, with a specific rotation value of −82° ($c = 1$, in chloroform)) and (*S*)-PCDC ($M_n = 24.5\ \mathrm{kg\,mol^{-1}}$, PDI = 1.17, with a specific rotation value of +82° in chloroform) was prepared by dissolving equal amounts of each enantiopure polycarbonate in chloroform. The addition of methanol to the homogeneous solution resulted in the immediate formation of a precipitate. Surprisingly, compared with the individual enantiomeric polymers the resultant precipitate has a lower solubility in common solvents such as chloroform and dimethyl sulfoxide. The same phenomenon was also observed in the PCEC stereocomplex formation from the 1:1 mixture of the amorphous (*R*)-PCEC ($M_n = 30.4\ \mathrm{kg\,mol^{-1}}$, PDI = 1.12, with a specific rotation value of −95° in chloroform) and (*S*)-PCEC ($M_n = 29.8\ \mathrm{kg\,mol^{-1}}$, PDI = 1.16, with a specific rota-

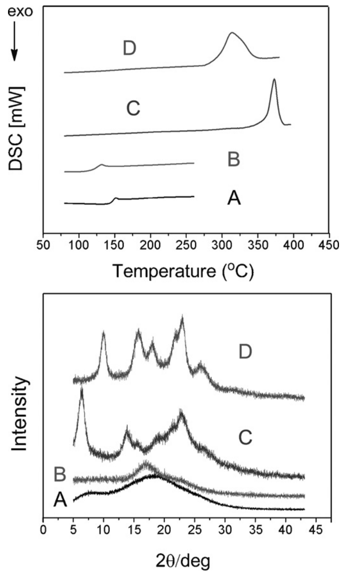

Figure 3. DSC thermograms (top) and WAXD profiles (bottom) of various polycarbonates. A) enantiopure isotactic (*S*)-PCDC; B) enantiopure isotactic (*S*)-PCEC; C) the 1:1 (mass ratio) mixture of (*R*)- and (*S*)-PCDCs; D) the 1:1 (mass ratio) mixture of (*R*)- and (*S*)-PCECs. All the samples were crystallized isothermally at 160 °C for 2 h, and samples in plots C and D were analyzed by FSC (top). The results of DSC and FSC analysis are given based on the second heating cycle.

tion value of +95° in chloroform). After drying, the resulting polymers were analyzed by DSC and the thermal properties were compared with the individual (*R*)- and (*S*)-enantiomer. Neither T_g nor T_m was observed in the normal DSC traces of both PCDC and PCEC stereocomplexes, significantly distinct from the individual enantiomers for which T_gs appeared at 150 and 130 °C, respectively. To confirm the crystallinity of the blends, fast-scan chip-calorimeter (FSC) measurement (Flash DSC) was performed for PCDC and PCEC stereocomplexes. Notably, a T_m of 314 °C was found for the PCEC stereocomplex (Figure 3, top, plot D). Especially, a quite sharp and high-melting endothermic peak at 373 °C was found for the PCDC stereocomplex, the highest T_m yet reported for this type of polymer (Figure 3, top, plot C). Moreover, samples of both enantiopure, isotactic polymers and a 1:1 mixture of the opposite enantiomers were further analyzed by wide-angle X-ray diffraction (WAXRD). The WAXRD study confirmed the formation of polycarbonate stereocomplexes with the presence of various crystalline diffraction peaks, whereas the individual (*R*)- and (*S*)-enantiomers are not crystalline in spite of the high isotacticity. For the 1:1 mixture of (*R*)-PCDC and (*S*)-PCDC, three diffraction peaks appear at 6.4°, 14.0°, and 22.7° ($d = 13.80$, 6.32, and 3.91), respectively, indicating a typical semicrystalline structure (Figure 3, bottom, plot C). Furthermore, the WAXRD study demonstrated that contrary to the enantiopure components, the 1:1 mixture of (*R*)-PCEC and (*S*)-PCEC was also crystalline with five crystalline diffraction peaks appearing at 10.1°, 15.8°, 18.3°, 23.0°, and 25.7° (Figure 3, bottom, plot D).

Although the structure of CDO and CEO is comparable with that of cyclohexene oxide (all bearing a six-membered ring unit) the highly isotactic PCDC and PCEC with 99 % *ee* proved to be amorphous. On the contrary, isotactic PCHC shows high levels of crystallinity. The huge difference in the solid aggregation (crystallization and melting behavior) of these isotactic polycarbonates stimulates us to explore the intrinsic reason between carbonate unit structure and its orderly aggregation crystallization. Since the chirality of the 1,2-diols produced from the hydrolysis of polycarbonates in the presence of an aqueous solution of sodium hydroxide is in agreement with their main-chain chirality, these 1,2-diols can respond to the structure information of the chiral carbonate unit of polymers. Therefore, after hydrolysis of the resulting polycarbonates with aqueous NaOH, we succeeded in isolating the corresponding diols in the crystal state (Figure 4). For (1*S*,2*S*)- or (1*R*,2*R*)-cyclohexane-1,2-diol, cyclohexane was more inclined to adopt a three-dimensional structure (known as the chair conformation) in order to reduce torsional strain (C1, C3, C5 in a plane, and C2, C4, C6 in another plane). There were two main conformational isomers for (1*R*,2*R*)-cyclohexane-1,2-diol or (1*S*,2*S*)-cyclohexane-1,2-diol, both of the hydroxy groups were in the equatorial positions to reduce the energy. However, this situation was different for (2*S*,3*S*)-1,2,3,4-tetrahydronaphthalene-2,3-diol. Its crystal showed that C1, C2, C5, and C6 were all in a plane, and there were also two main conformational isomers for the *trans*-disubstituted products. To reduce torsional strain, both of the hydroxy groups were all in the equatorial positions. The crystal of (1*S*,2*S*)-cyclohex-4-ene-1,2-diol is similar with (2*S*,3*S*)-1,2,3,4-tetrahydronaphthalene-2,3-diol. X-ray single-crystal analysis shows that there are two conformational isomers for *trans*-(*S*,*S*)-disubstituted cyclohexane and cyclohexene ring, and the substituted groups are more inclined to anchor at equatorial positions for both of the *trans*-(*S*,*S*)-disubstituted substrate (Figure 4).

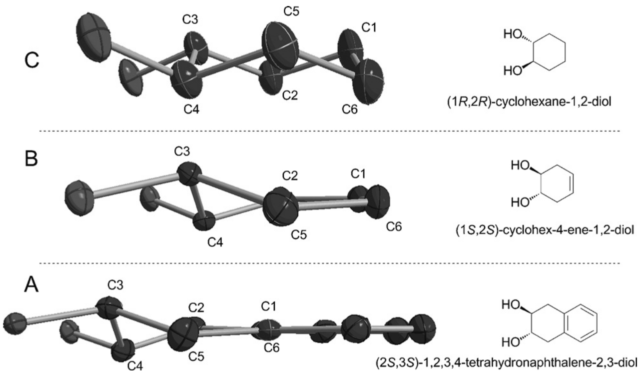

Figure 4. Molecular structure of various chiral diols. A) (2*S*,3*S*)-1,2,3,4-tetrahydronaphthalene-2,3-diol; B) (1*S*,2*S*)-cyclohex-4-ene-1,2-diol; and C) (1*R*,2*R*)-cyclohexane-1,2-diol, produced from the hydrolysis of the corresponding isotactic polycarbonates (*S*)-PCDC, (*S*)-PCEC, and (*R*)-PCHC, respectively.

Due to the structure comparability of PCDC and PCEC, we further explored the possibility for the formation of hetero-stereocomplexed polycarbonates. Just like their homo-stereocomplexes, the 1:1 mixture of (*S*)-PCEC and (*R*)-PCDC or (*R*)-PCEC and (*S*)-PCDC show lower solubility in organic solvents, which is significantly different for the individual enantiomerically pure polymers. WAXRD clearly shows the existence of multicrystalline diffraction peaks, confirming the formation of crystalline stereocomplexes. For example, the 1:1 mixture of (*S*)-PCEC and (*R*)-PCDC has four crystalline diffraction peaks appearing at 7.3°, 8.0°, 15.3°, and 22.4° (Figure 5, bottom, plot B). Notably, the crystallization behavior is different from that of the stereocomplexes of (*R*)-/(*S*)-PCEC and (*R*)-/(*S*)-PCDC. It is a rare example for stereocomplex formation from the amorphous polymers from different families having opposite stereoregular configurations. In contrary, no cocrystallite formation between (*S*)-PCEC and (*S*)-PCDC chains with the same configurations was observed. Due to the good miscibility of (*S*)-PCEC and (*S*)-PCDC chains, their mixture has only one T_g of 135 °C, between the T_gs of the individual enantiomers having the identical configurations (Figure 5, top, plot A). However, (*S*)-PCEC and (*R*)-PCDC blends having the opposite configurations show a T_m of 320 °C from FSC analysis, demonstrating it was a new type of crystalline CO_2-based polycarbonate (Figure 5, top, plot B).

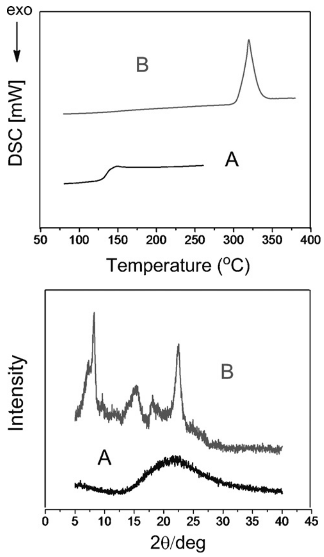

Figure 5. DSC thermograms (top) and WAXD profiles (bottom) of various polycarbonates. A) the 1:1 (molar ratio) mixture of (*S*)-PCEC and (*S*)-PCDC; B) the 1:1 (molar ratio) mixture of (*S*)-PCEC and (*R*)-PCDC. All samples were crystallized isothermally at 160 °C for 2 h, and the sample in plot B was analyzed by FSC (top). The results of DSC and FSC analysis are given based on the second heating cycle.

Furthermore, two novel crystalline hetero-stereocomplexed polycarbonates were found by mixing amorphous (*S*)-PCEC or (*S*)-PCDC with crystalline (*R*)-PCHC in equivalent amounts. The polymer stereocomplex of enantiomeric PCDC and PCHC with opposite configuration shows three main crystalline diffraction signals at 8.2°, 15.2°, and 22.2° (Figure 6, plot B). Moreover, the polymer stereocomplex of (*S*)-PCEC and (*R*)-PCHC has two large crystalline diffraction signals at 9.6° and 21.7° along with a number of smaller peaks between them (Figure 6, plot C). It should be noted that in comparison to the component enantiomeric polymers or their homo-stereocomplexes, the crystalline behaviors of the two hetero-stereocomplexes are completely different, indicating the formation of new crystalline materials.

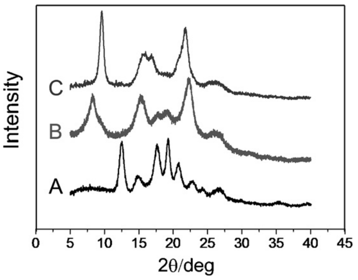

Figure 6. WAXD profiles of various polycarbonates. A) enantiopure isotactic (*R*)-PCHC; B) the 1:1 (molar ratio) mixture of (*S*)-PCDC and (*R*)-PCHC; C) the 1:1 (molar ratio) mixture of (*S*)-PCEC and (*R*)-PCHC. The samples were crystallized isothermally at 160 °C for 2 h.

In conclusion, highly isotactic CO_2-based polycarbonates from *meso*-epoxides (1,4-dihydronaphthalene oxide and 1,2-epoxy-4-cyclohexene) with perfectly alternating structure and 99 % enantioselectivity, proved to be typically amorphous materials, possessing T_gs of 150 and 130 °C, respectively. Mixing of these amorphous enantiomeric polymers with identical chemical compositions and opposite configurations in equivalent amounts afforded the crystalline stereocomplexed polycarbonates. Notably, this is the first report on the formation of crystalline hetero-stereocomplexes from opposite enantiomers of amorphous polymers with different chemical compositions. The present study is expected to open up a new way to prepare various semicrystalline materials with a wide variety of physical properties and degradability. Further exploration will focus on the preparation of various novel semicrystalline polycarbonates and their potential application in biomedical fields.

Keywords: carbon dioxide · cocrystallization · *meso*-epoxides · polycarbonates · polymer assembly

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