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VIP **Polymer Stereocomplexes** **Very Important Paper**

Crystalline Stereocomplexed Polycarbonates: Hydrogen-Bond-Driven Interlocked Orderly Assembly of the Opposite Enantiomers**

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Abstract: *Four novel crystalline stereocomplexed polymers are formed by mixing isotactic (R)- and (S)-polycarbonates in 1:1 mass ratio. They show the enhanced thermal stability and new crystalline behavior, significantly distinct from the component enantiomer. Two stereocomplexed CO_2-based polycarbonates from meso-3,4-epoxytetrahydrofuran and 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane have high melting temperatures of up to 300°C, about 30°C higher than the individual enantiomers. Isotactic (R)- or (S)-poly(cyclopentene carbonate) and poly(cis-2,3-butene carbonate) are typical amorphous polymeric materials, however, upon mixing both enantiomers together, a strong interlocked interaction between polymer chains of opposite configuration occurs, affording the crystalline stereocomplexes with melting temperatures of about 200°C and 180°C, respectively. A DFT study suggests that the driving force forming the stereocomplex is the hydrogen-bonding between carbonate units of the opposite enantiomers.*

The physical properties of a polymer are determined not only by the structure of the monomer, the molecular weight, and polydispersity of the polymer, but also by the relative stereochemistry (the spatial arrangement of atoms or groups in a polymeric unit) of adjacent locations in the polymeric chains.[1] A representative example is the much-studied polylactide. As a result of the presence of backbone stereocenters, the tacticity (stereo-microstructure) has a drastic effect on the polymer's thermal and mechanical properties. The amorphous atactic polylactide has a glass transition temperature (T_g) of only about 60°C, and enantiopure (D)- or (L)-polymer has a melting temperature $T_m = 180$°C, while heterotactic polylactide undergoes very slow crystallization to yield a semicrystalline polymer with a low T_m of 120°C. Interestingly, if enantiopure (D)- and (L)-polylactides are mixed in equivalent amounts they form a novel stereocomplex with an enhanced T_m of 230°C, which is about 50°C higher than for the individual enantiomers.[2–5] Degradable polycarbonates produced from the alternating copolymerization of CO_2 and epoxides, there also display the interesting stereochemistry-based properties, which depend on the stereoselective ring-opening of epoxides.[6–11] In a recent contribution, Nozaki and co-workers disclosed a novel stereogradient poly(propylene carbonate)s (PPCs) consisting of two enantiomeric structures on each end, prepared by enantiopure metal-complex-mediated regio- and enantioselective copolymerization of racemic propylene oxide with CO_2.[12] The iso-enriched stereogradient PPCs have higher thermal decomposition temperatures than the typical PPCs, suggesting the formation of a stereocomplex between two enantiopure components of the polymeric main chains. In 2012, we succeeded in synthesizing highly isotactic poly(cyclohexene carbonate) (PCHC) by the desymmetrization copolymerization of CO_2 and *meso* cyclohexene oxide, and it was found that isotacticity has the critical influence on the crystallinity and only copolymers with a isotacticity of more than 90% are crystallizable.[13] Notably, a PCHC stereocomplex with an enhanced T_m was discovered to be formed by mixing isotactic (*R*)-PCHC and (*S*)-PCHC in a 1:1 mass ratio.[14] The crystallization behavior of the stereocomplexed polycarbonate is distinct from that of the sole (*R*) or (*S*) configuration polymer. More recently, we developed a chiral catalyst system based on a biphenol-linked dinuclear Co^{III} complex, which exhibited excellent activity, unprecedented enantioselectivity (> 98% *ee*), and molecular-weight control for the alternating copolymerization of CO_2 with various *meso*-epoxides under mild reaction conditions.[15] Moreover, several crystalline CO_2-based polycarbonates, such as from *meso*-3,4-epoxytetrahydrofuran (COPO) and 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (CXO) with good thermal stability were discovered.[16,17] With these enantiopure and isotactic polycarbonates in hand, we are interested to systematically explore the interaction between opposite configuration polymers. Herein, we report the formation of various crystalline stereocomplexes from both crystallizable and amorphous isotactic polycarbonates (Figure 1).

The optically active isotactic polycarbonates with chiral (*R*,*R*)- or (*S*,*S*)-*trans*-1,2-diol units in the main chain were prepared by enantiopure dinuclear Co^{III}-complex mediated desymmetrization copolymerization of CO_2 with *meso*-epoxides.[15] Since isotactic CO_2/CXO copolymer (PCXC) is easily crystallizable, it was chosen as a model CO_2-based polycarbonate for testing the interaction of opposite configuration polymers.[16] A 1:1 mixture of (*R*)-PCXC ($M_n = 18.1\ \mathrm{kg\,mol^{-1}}$, polydispersity index (PDI) = 1.15) and (*S*)-PCXC ($M_n = 17.5\ \mathrm{kg\,mol^{-1}}$, PDI = 1.18) was prepared by dissolving equal amounts of each enantiopure polycarbonate in DMSO solvent. The addition of methanol to the homogeneous solution resulted in the immediate formation of a precipitate. Interestingly, the precipitate has no solubility in DMSO and

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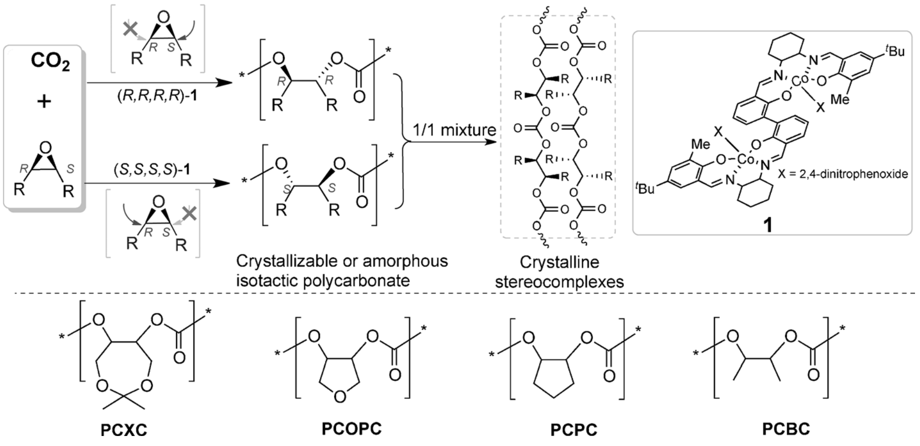

Figure 1. Enantioselective copolymerization of CO_2 and various *meso*-epoxides to enantiopure isotactic polycarbonates, and further formation of crystalline stereocomplexes.

other solvents, which is distinct from the component polymers. To our surprise, neither T_g nor T_m was observed in the DSC (differential scanning calorimetry) trace of the precipitate, while a quite sharp and high-melting endothermic peak is found at 242 °C with $\Delta H_m = 29.89\ \mathrm{J\,g^{-1}}$ for isotactic (*R*)- or (*S*)-PCXC (Figure 2, top). Furthermore, the wide-angle X-ray diffraction (WAXD) analysis of these samples was performed (Figure 2, bottom). No diffraction was observed for the corresponding atactic copolymer, confirming its amorphous feature. For highly isotactic polycarbonates, sharp diffraction peaks were observed at 2θ values of 11.8°, 14.3°, 16.9°, and 20.4° ($d = 7.49$, 6.19, 5.24, and 4.35, respectively) (Figure 2, bottom, plot B), demonstrating that the isotactic PCXC is a typical semi-crystalline polymer. The 1:1 mixture of (*R*)- and (*S*)-PCXCs has the different diffraction peaks appearing at 2θ equal to 6.4°, 13.3°, 16.0°, 17.9°, 20.5°, and 23.0° ($d = 13.80$, 6.65, 5.53, 4.95, 4.33, and 3.86, respectively; Figure 2, bottom, plot C). This result suggests the formation of a stereocomplex with a new crystalline structure, that is different from that of the sole configuration PCXC. The lack of the melting transition in the DSC plots is attributed to a T_m that is higher than its decomposition temperature (Figure 2, top, plot C).

As expected, the formation of a stereocomplex from the 1:1 mixture of (*R*)-PCOPC (COPO/CO_2 copolymer) ($M_n = 10.0\ \mathrm{kg\,mol^{-1}}$, PDI = 1.14) and (*S*)-PCOPC ($M_n = 10.9\ \mathrm{kg\,mol^{-1}}$, PDI = 1.16) was confirmed by DSC and WAXD analyses (Figure 3). It is clearly seen that the 1:1 mixture of (*R*)- and (*S*)-PCOPCs gives a single endothermic peak around 300 °C with $\Delta H_m = 49.70\ \mathrm{J\,g^{-1}}$ (Figure 3, top, plot C), significantly higher than the T_m of 271 °C with $\Delta H_m = 32.24\ \mathrm{J\,g^{-1}}$ for (*R*)- or (*S*)-PCOPC sample (Figure 3, top, plot B), indicating a very high degree of crystallinity. WAXD also shows a different pattern, as can be seen in Figure 3 (bottom). The diffraction peaks appear at 2θ around 18.1°, 19.9°, and 23.2° for the individual (*R*)- or (*S*)-PCOPC enantiomer, whereas the 1/1 blend polymer has the diffraction peaks appearing at 2θ equal to 16.3°, 18.9°, 20.9°, and 23.6°. Both DSC and WAXD studies support the formation of a polymer stereocomplex with a crystalline structure entirely different from that of the component polymers.

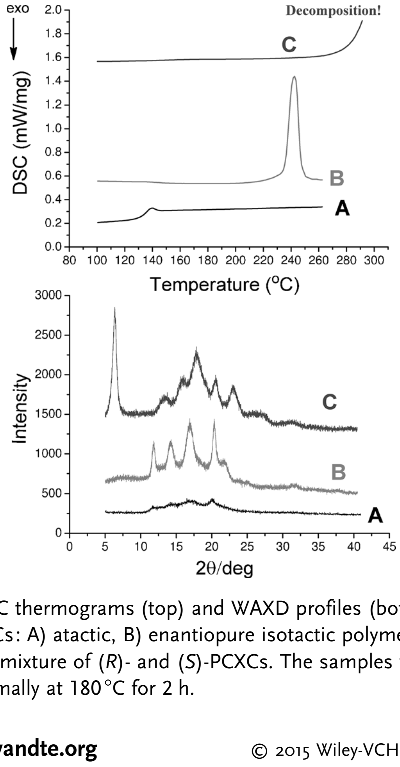

Figure 2. DSC thermograms (top) and WAXD profiles (bottom) of various PCXCs: A) atactic, B) enantiopure isotactic polymer, C) the 1:1 (mass ratio) mixture of (*R*)- and (*S*)-PCXCs. The samples were crystallized isothermally at 180 °C for 2 h.

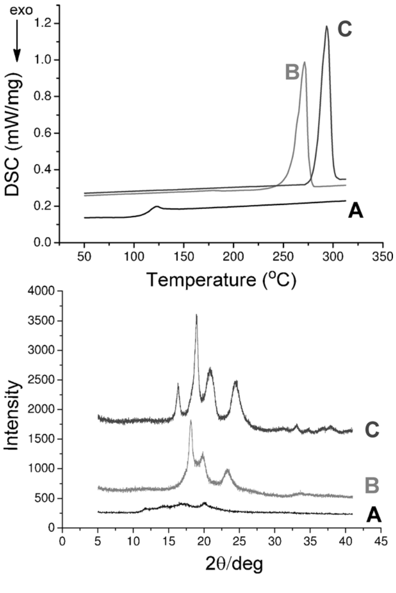

Figure 3. DSC thermograms (top) and WAXD profiles (bottom) of various PCOPCs: A) atactic, B) enantiopure isotactic polymer, C) the 1:1 (mass ratio) mixture of (*R*)- and (*S*)-PCOPCs. The samples were crystallized isothermally at 180 °C for 2 h and undergo an end-capping reaction.

In previous studies, we have demonstrated that highly isotactic PCHC and PCOPC are easy to be crystallized under certain conditions.[13,17] Nevertheless, highly isotactic poly(-cyclopentene carbonate) (PCPC) with over 99% *ee* obtained from the asymmetric copolymerization of CO_2 with *meso*-cyclopentene oxide proved to be amorphous and has a T_g of 85 °C, though the epoxide used has a comparable structure to cyclohexene oxide and COPO. We were delighted to find that in the DSC trace of the 1:1 mixture of (*R*)-PCPC ($M_n = 29.2\ \mathrm{kg\,mol^{-1}}$, PDI = 1.20) and (*S*)-PCPC ($M_n = 29.8\ \mathrm{kg\,mol^{-1}}$, PDI = 1.24), there appeared a sharp melting endothermic peak at 199 °C with $\Delta H_m = 35.68\ \mathrm{J\,g^{-1}}$ (Figure 4, top, plot B). Moreover, WAXD investigation further gives the evidence of cocrystallization of the 1:1 blend polymers. Five diffraction peaks appear at 2θ around 15.3°, 18.0°, 19.6°, 21.2° and 24.1 respectively (Figure 4, bottom, plot B). Similarly, the semi-crystalline stereocomplex was also discovered to be formed from the 1:1 mixture of the amorphous isotactic (*R*)-poly(*cis*-2,3-butene carbonate)s ($M_n = 38.2\ \mathrm{kg\,mol^{-1}}$, PDI = 1.19) and (*S*)-poly(*cis*-2,3-butene carbonate)s ($M_n = 39.3\ \mathrm{kg\,mol^{-1}}$, PDI = 1.20; PCBC) in dichloromethane solvent. A strong melting endothermic peak at 177 °C with $\Delta H_m = 47.73\ \mathrm{J\,g^{-1}}$ can be seen in the DSC trace of the 1:1 blend polymer (Figure 4, top, plot D), while only a T_g of 73 °C appears in that of enantiopure isotactic PCBC sample, implying its amorphous structure. Also, multi diffraction peaks are observed in the 1:1 blend mixture (Figure 4, bottom, plot D).

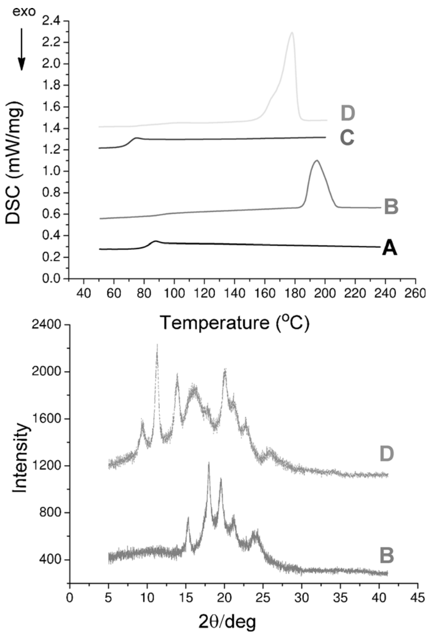

Figure 4. DSC thermograms (top) and WAXD profiles (bottom) of various PCPCs and PCBCs: A) enantiopure isotactic PCPC, B) the 1:1 (mass ratio) mixture of (*R*)- and (*S*)-PCPCs, C) enantiopure isotactic PCBC, and D) the 1:1 (mass ratio) mixture of (*R*)- and (*S*)-PCBCs. The PCPC samples were crystallized isothermally at 180 °C for 2 h and PCBC samples were crystallized isothermally at 140 °C for 2 h.

Stereocomplexation is the stereoselective interaction between two opposite enantiomeric polymers, just like small molecule racemates, where pairs of enantiomers preferably crystallize in a 1:1 ratio in the unit cell. The interlocked arrangement of two opposite-configuration carbonate units results in the orderly assembly of polymeric chains. The driving force of forming the stereocomplex might be ascribed to the formation of hydrogen bonds between each oxygen atom of carbonyl groups of one enantiomer and the hydrogen atom on the methine CH group of the other stereoisomer. To get a better understanding of the interaction between the two opposite enantiomeric polymers, density functional theory (DFT) calculations were performed using the stereocomplexed PCPC as a model polymer. For simplifying the calculation, four carbonates units with opposite configuration were used for structure optimization (Figure 5). It was found that the distance between the oxygen atom of the carbonyl group in one stereoisomer and the hydrogen atom on the methine group in the other was approximately 2.3 Å, suggesting the formation of a hydrogen bond. Nevertheless, the hydrogen-bonding interaction does not exist between every carbonate unit of two opposite enantiomeric polymer chains because of the sterically crowded environment. Moreover, (*S*)-and (*R*)-PCBC, (*S*)- and (*R*)-PCOPC were studied by DFT calculations, and the existence of the hydrogen-bonding interaction was confirmed for the optimized stable structures (Figures S8 and S9 in the Supporting Information). When a carbonate unit of one enantiomer chain interacts with that of the opposite enantiomer chain, the adjacent carbonate unit will interact with a carbonate unit of the other opposite enantiomer chain, so the 'layer shape' might be the main structure for the stereocomplexed polycarbonates (Figure 6 and Figure S10 in the Supporting Information). However, we could not rule out other interactions, such as the compact package of two opposite enantiomeric polymers being responsible for the formation of stereocomplexes, just like stereocomplexed polylactides.[18,19]

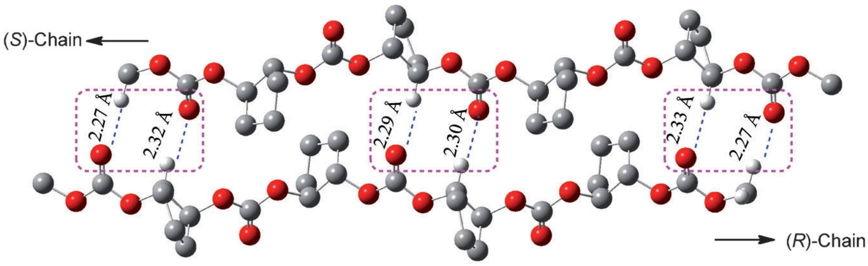

Figure 5. Optimized stable structure from (*R*)-PCPC and (*S*)-PCPC chains (hydrogen atoms was omitted for clarity excepted for hydrogen bonding). C gray, O red, H white.

In conclusion, various crystalline stereocomplexes with enhanced decomposition temperatures were found to be formed in the blend of equivalent isotactic (*R*)- and (*S*)-polycarbonates. Notably, two of them originate from amorphous enantiopure polymers. They are rare examples of amorphous polymers that become crystalline upon stereocomplexation with the opposite configuration polymers.

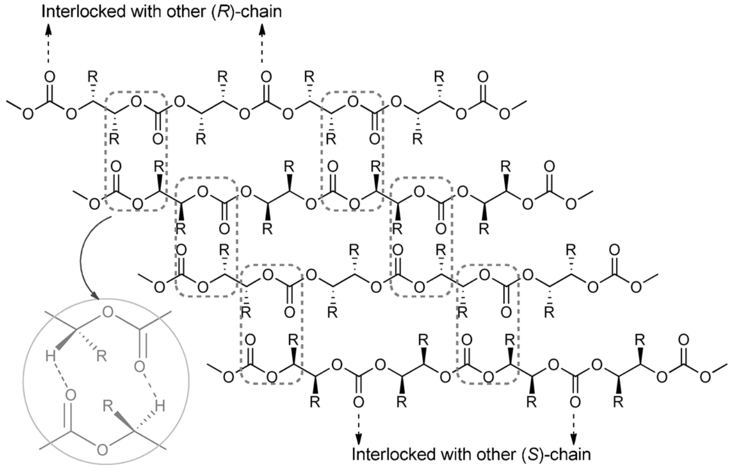

Figure 6. "Layer shape" structure of the stereocomplexed polycarbonates.

Further efforts will focus on the crystallization kinetics of these stereocomplexed CO_2-based polycarbonates and their potential applications in biomedical and pharmaceutical fields.

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Keywords: carbon dioxide · crystalline · enantiopure polycarbonates · epoxides · polymer stereocomplexes

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