

Rapid Communication

STEREOREGULAR POLY(CYCLOHEXENE CARBONATE)S: UNIQUE CRYSTALLIZATION BEHAVIOR*

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Abstract An example of crystalline CO₂-based polymer from the asymmetric alternating copolymerization of CO₂ and cyclohexene oxide is reported. Isotacticity of poly(cyclohexene carbonate) (PCHC) has the critical influence on the crystallinity, and only copolymers with a isotacticity of more than 90% are crystallizable. The stereoregular PCHC is a typical semi-crystalline thermoplastic, and possesses a high melting point (T_m) of 215–230°C and a decomposition temperature of *ca.* 310°C. The spherulitic morphology of (*R*)-PCHC grows in a clockwise spiral from a center, and that of (*S*)-PCHC is a counterclockwise spiral, while the stereocomplex of (*S*)-PCHC/(*R*)-PCHC (1/1 mass ratio) presents lath-like dendritic crystal. The novel crystalline CO₂-based polycarbonate represents a rare example of optically active polymers with unique crystallization behavior. Our findings reflect the critical influence of stereoregularity on the crystallization for this kind of polymeric materials, and may lead to developments of thermal-resistance CO₂ copolymers for application in engineering thermoplastics.

Keywords: Carbon dioxide; Poly(cyclohexene carbonate); Stereoregular; Crystallization; Stereocomplex.

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Transformation of CO₂ into degradable polycarbonates by the alternating copolymerization with epoxides represents one of the most well-studied and innovative technologies for potential large-scale utilization of CO₂ in chemical synthesis^[1–3]. In the recent decade, we have witnessed tremendous progress in catalyst activity for CO₂/epoxides copolymerization^[4–11]. Especially, homogeneous catalyst systems based on salenCo(III) complexes show impressive characteristics, they may exhibit immortal polymerization (a living polymerization) with excellent regio- and stereo-chemistry control and unprecedented activities at very low catalyst loading and/or low CO₂ pressures, even 0.1 MPa^[12–20]. Unfortunately, all previously reported CO₂-based polycarbonates are amorphous, and their low thermal degradation resistance makes them difficult to use as structural materials. It is generally known that more than 80% commodity polymers are crystallizable^[21–23]. In the manufacturing procedure of a polymer, the physical and mechanical properties of injection moulding products mainly depend on technological parameters, the polymer's crystal structure and its crystallinity^[24–26]. Herein, we report the first

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example of crystalline CO₂-based polymers from the stereo-selectively alternating copolymerization of CO₂ and cyclohexene oxide with the use of enantiopure Co(III)-based catalysts (Fig. 1). The stereoregular poly(cyclohexene carbonate) (PCHC), which has a relatively high T_m of 215–230°C and decomposition temperature of *ca.* 310°C. The crystallization properties such as melting behavior, microscopic phase structure and crystal morphology of these crystalline PCHCs were investigated using differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), atomic force microscopy (AFM) and transmission electron microscopy (TEM).

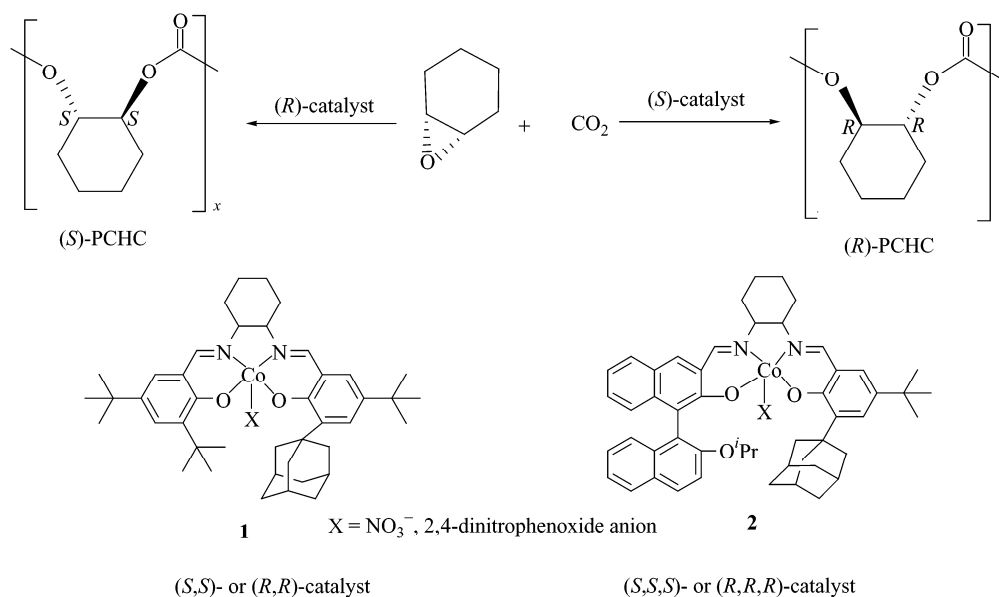


Fig. 1 Preparing stereoregular poly(cyclohexene carbonate)s by asymmetric alternating copolymerization of CO₂ and cyclohexene oxide

For any given polymer, the experimentally observed physical properties are determined mainly by the relative stereochemistry (the spatial arrangement of atoms or groups in a polymeric unit) of adjacent locations in the polymeric chains^[27]. In most cases, the crystallization behavior of a polymer is mainly dependant on its stereoregularity. Stereoregular PCHCs were prepared by asymmetric alternating copolymerization of CO₂ and *meso*-cyclohexene oxide with the use of enantiopure metal catalysts. Because the nucleophilic ring opening of a *meso*-epoxide proceeds with inversion at one of the two chiral centers, a successful asymmetric ring opening by a chiral catalyst or reagents can give optically active polycarbonates with main-chain chirality concerning an (*R,R*)-or (*S,S*)-*trans*-1,2-diol unit. In 1999, Nozaki and co-workers described the first example of the asymmetric copolymerization of CO₂ and cyclohexene oxide using an equimolar mixture of Et₂Zn and (*S*)- α,α -diphenyl(pyrrolidin-2-yl)methanol as a chiral catalyst system, affording the polycarbonate with moderate enantioselectivity (30%–70% ee)^[28]. Subsequently, Coates group reported the use of well-defined hybrid β -imine oxazoline zinc-based catalysts for this reaction, which showed similar enantioselectivity, but higher activity and controlled molecular weight^[29]. The stereoregularity of the resultant polycarbonate is easily determined by ¹³C-NMR spectra of carbonyl region signals or/and the enantiomeric excess (ee) of the corresponding cyclohexane-1,2-diol after hydrolysis with aqueous NaOH. Based on our preliminary studies of the asymmetric alternating copolymerization of aliphatic epoxides and CO₂^[30, 31], we succeeded in designing highly stereoregular catalyst systems regarding unsymmetric enantiomerically pure cobalt(III) complexes, and further synthesized various optically active polycarbonates: (*R*)-PCHC-92 (*RR:SS* ratio in the resultant polycarbonate is 92:8, M_n = 10200, M_w/M_n = 1.18), (*R*)-PCHC-98 (*RR:SS* = 98:2, M_n = 9200, M_w/M_n = 1.14) and (*S*)-PCHC-98 (*RR:SS* = 2:98, M_n = 8600, M_w/M_n = 1.17). ¹H-NMR analysis indicates that these polycarbonates

all have more than 99% carbonate linkages. ^{13}C -NMR spectra in carbonyl region of the stereoregular PCHCs demonstrate their isotactic structure, with the near disappearance of the syndiotactic diads ($\delta = 153.3\text{--}151.1$, see Supporting Information, Fig. S1).

The crystallization and melting behavior of the PCHCs were studied by means of DSC in a flowing-nitrogen atmosphere. Figure 2 shows the DSC thermograms of PCHC with various degrees of isotacticity in the second heating cycle. Only a single glass transition peak was observed at around 115°C for the atactic PCHC, demonstrating that this polymer is completely amorphous. The isotacticity of PCHC has the critical influence on its crystallinity. It was found that the samples with less than 90% isotacticity did not show any crystallization. We were delighted to find that the (*R*)-PCHC-92 gave a T_g of 122°C and a very small melting endothermic peak at 207°C with the melting enthalpy of (ΔH_m) 3.92 J/g, indicating a very low degree of crystallinity. Regarding the highly isotactic polymer (*R*)-PCHC-98, one should first notice from the DSC trace that the T_g peak has disappeared, while a quite sharp and high crystallization endothermic peak is now found at 216°C with $\Delta H_m = 22.50$ J/g. The result implies that the crystallization ability of PCHC is greatly enhanced with the increase in isotacticity.

It has been observed for polylactide systems that a stereocomplex formed by the self assembly of optically active polymers with opposite enantiomeric configurations showed different thermal properties and crystallization behaviour compared to its parent polymers^[32, 33]. A similar increase in melting point was also observed for the (*R*)-PCHC-98/(*S*)-PCHC-98 blends (1/1 mass ratio). In comparison with that of PCHC with a singular configuration, the crystallization endothermic peak of the blend increases to 227°C with $\Delta H_m = 29.70$ J/g using the same crystallization conditions (Fig. 2, curve d). This indicates that the blends of the PCHCs with two opposing configurations formed a stereocomplex with a new and distinct crystalline structure. The following wide angle X-ray diffraction (WAXD) studies further provide positive evidence to this point.

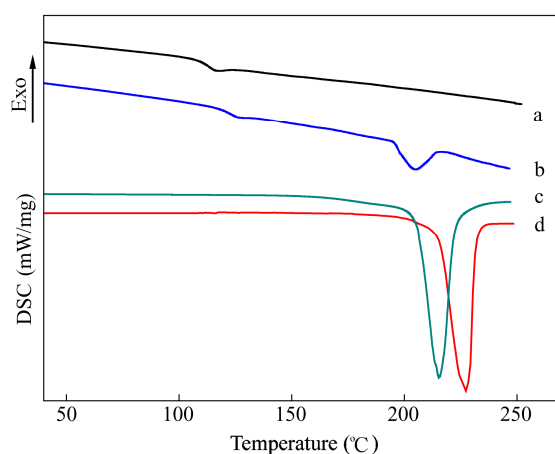


Fig. 2 DSC thermograms of various poly(cyclohexene carbonate)s: (a) atactic PCHC, (b) (*R*)-PCHC-92, (c) (*R*)-PCHC-98 and (d) blend of (*R*)-PCHC-98/(*S*)-PCHC-98, 1/1 mass ratio. The samples were crystallized isothermally at 180°C for 60 min.

Figure 3 shows the WAXD profiles of atactic PCHC, (*R*)-PCHC-92, (*R*)-PCHC-98 and the blend of (*R*)-PCHC-98/(*S*)-PCHC-98 (1/1 mass ratio) which were crystallized isothermally at 180°C for 60 min and measured at room temperature in air atmosphere. No diffraction was observed for the atactic PCHC, confirming its amorphous feature. On the contrary, for (*R*)-PCHC-98 sample, sharp diffraction peaks were observed at 2θ values of 12.2° , 17.9° , 19.0° and 20.4° , demonstrating that the isotactic PCHC is a typical semicrystalline polymer. The diffraction profile for (*S*)-PCHC-98 sample is identical with that of (*R*)-PCHC-98. Surprisingly, the blend of (*S*)-PCHC-98/(*R*)-PCHC-98 has different diffraction peaks appearing at 2θ equal to 8.6° , 17.9° and

21.5° (Fig. 3, curve d), while the peaks at 12.2°, 19.0° and 20.4° have disappeared. This result suggests the formation of a stereocomplex with a new crystalline structure, being different from that of the sole configuration PCHC.

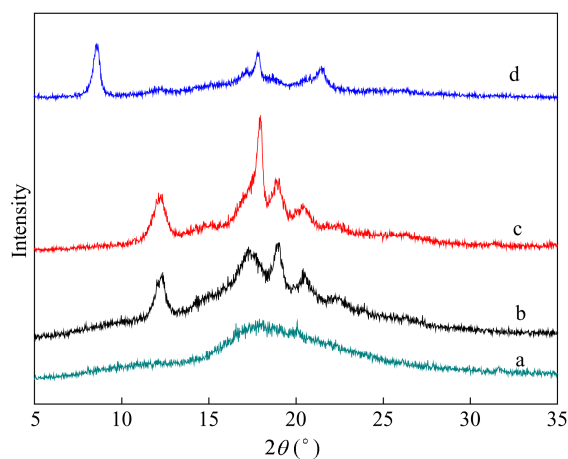


Fig. 3 WAXD profiles of various poly(cyclohexene carbonate) samples: (a) atactic PCHC, (b) (*R*)-PCHC-92, (c) (*R*)-PCHC-98 and (d) blend of (*R*)-PCHC-98/(*S*)-PCHC-98, 1/1 mass ratio

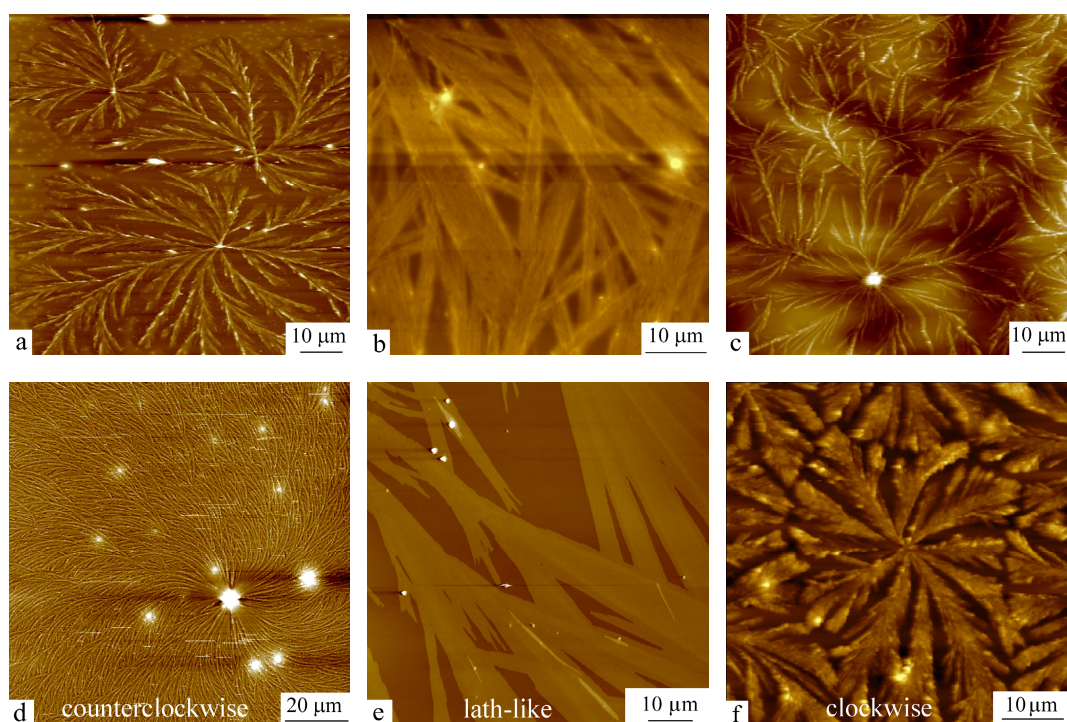


Fig. 4 AFM height images of different helical chirality samples crystallized on fresh cleaved mica substrate: (a) (*S*)-PCHC-98 sample crystallized at 150°C for 48 h, (b) blend of (*R*)-PCHC-98/(*S*)-PCHC-98 (1/1 mass ratio) crystallized at 170°C for 24 h, (c) (*R*)-PCHC-98 sample crystallized at 150°C for 24 h, (d) (*S*)-PCHC-98 sample crystallized at 130°C for 24 h, (e) blend of (*R*)-PCHC-98/(*S*)-PCHC-98 (1/1 mass ratio) crystallized at 170°C for 24 h and (f) (*R*)-PCHC-98 sample crystallized at 170°C for 24 h

To further reveal the crystallization behavior of optically active PCHCs, detailed morphologies were obtained by AFM observations (Fig. 4). The samples were prepared by melt-crystallization isothermally at the indicated temperatures for sufficient time to ensure crystallization. For (*S*)-PCHC-98, as shown in Figs. 4(a) and 4(d), spherulites have been clearly observed in the AFM height images. It is worthy to note that the lamellae or lamellar aggregates preferentially bend anti-clockwise. On the other hand, the crystal feature of (*R*)-PCHC-98 isothermally crystallized at 150°C for 24 h presents an absolutely different enantiomeric form. As shown in Fig. 4(c), a clockwise rotated spherulite can be clearly observed. In particular, with careful inspection, it can be found that the edges of other spherulites also have the same feature of clockwise rotation. Also, height AFM images obtained at 170°C clearly confirmed the lamellae or lamellar aggregates bending direction (Fig. 4f). To our surprise, the morphological feature of the stereocomplex of (*S*)-PCHC-98/(*R*)-PCHC-98 (1/1 mass ratio) changes dramatically. The height AFM image of the stereocomplex that had been isothermally crystallized at 170°C for 24 h is shown in Figs. 4(b) and 4(e). Unlike its parent polymers, the stereocomplex presents a lath-like dendritic crystal, which is very different from the bending feature observed for both the (*S*)-PCHC-98 and (*R*)-PCHC-98. Moreover, such uniqueness of crystal morphology and structure were also observed by transmission electron micrograph (TEM) (Supporting Information, Fig. S2).

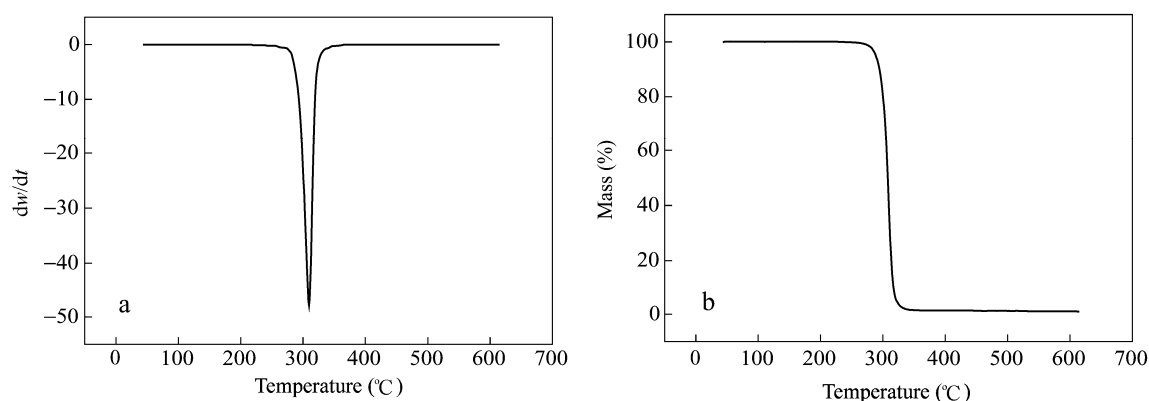


Fig. 5 The thermolysis curve of (*R*)-PCHC-98

In summary, we report the first example of crystalline CO₂-based polymers that have been prepared from the asymmetric alternating copolymerization of CO₂ and cyclohexene oxide. Resembling bisphenol-A polycarbonate (BPA-PC), the isotactic poly(cyclohexene carbonate) (PCHC) is a typical semi-crystalline thermoplastic, and possesses a high T_m of 216°C and decomposition temperature of *ca.* 310°C. A PCHC stereocomplex with an enhanced T_m of 227°C was found to be formed in the blend of equivalent (*R*)-PCHC and (*S*)-PCHC. The crystallization behavior of the stereocomplex polycarbonate is distinct from that of the sole (*R*) or (*S*) configuration polymer. The novel crystalline CO₂-based polycarbonate represents a rare example of optically active polymers with unique crystallization behavior. More importantly, these crystalline polycarbonates display excellent thermal performance with one decomposition temperature of 310°C (Fig. 5) far higher than those of traditional CO₂/epoxides copolymers, allowing these CO₂-based materials to be used as environmentally friendly engineering thermoplastics.

SUPPORTING INFORMATION

General experimental procedures including the synthesis of various stereoregular poly(cyclohexene carbonate)s, characteristics of enantiopure cobalt(III) complexes, as well as characteristics of stereoregular poly(cyclohexene carbonate)s

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