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Unveiling chain–chain interactions in CO_2-based crystalline stereocomplexed polycarbonates by solid-state NMR spectroscopy and DFT calculations

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ABSTRACT

CO_2-based stereocomplexed polycarbonates derived from the intermolecularly interlocked interaction between the enantiopure polymers with the opposite configuration exhibit high crystallinity, excellent thermal and mechanical stabilities. Deep insights into the mechanism of stereocomplexation are of particular importance to the design and manufacture of new promising and sustainable polycarbonates with enhanced physicochemical properties. Our solid-state NMR experiments linking with DFT computations clearly reveal the specific chain–chain interactions in a typical stereocomplexed poly (4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0] octane carbonate) (PCXC). ^{13}C CP/MAS NMR, ^{1}H DUMBO MAS NMR and $^{13}C/^{1}H$ relaxation-time measurements indicate that the formation of stereocomplex reduces the local mobilities of carbonyl, methine and methylene groups in each chain of PCXC significantly. Through a combination of two-dimensional ^{1}H–^{13}C HETCOR NMR and DFT calculation analysis, the *cis*-/*trans*- conformations and packing models of PCXC chains in the amorphous, enantionpure isotactic and stereocomplexed polycarbonates are identified. The splitting of ^{13}C and ^{1}H NMR chemical shifts of methine groups in the backbone carbon region demonstrates the ordered interlock interactions between the *R*- and *S*- chain in the stereocomplexed PCXC.

1. Introduction

Degradable polycarbonates produced from the alternating copolymerization of CO_2 and epoxides represent a kind of very promising sustainable polymers, and begin to be commercialized recently [1–4]. However, the amorphous properties and low glass-transition-temperature (T_g) of CO_2 copolymers significantly hinder their practical applications. To address these issues, enhancing the stereoregularity of CO_2 copolymer can elevate the T_g and even get some crystalline polycarbonates with isotacticity of more than 90% [5–7]. Moreover, the formation of the stereocomplex between two opposite enantiopure polymer chains can further increase the crystallization of polymers because the stereocomplex acts as a single macromolecule to form crystals [8–11]. Consequently, it has higher thermal resistance than the enantiopure components. Thanks to the successful synthesis of enantionpure polycarbonates recently reported by Coates's group and our group, polycarbonates such as poly (limonene carbonate) (PLC), poly (cyclohexene carbonate) (PCHC), poly(1,4-dihydronaphthalene carbonate) (PCDC), poly (*meso*–3,4-epoxytetrahydrofuran carbonate) (PCOPC) and poly (4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane carbonate) (PCXC) can form crystalline or show enhanced melting temperature (T_m) by mixing isotactic *R*- and *S*- chain in a 1:1 mass ratio [12–15]. Up to now the catalytic syntheses of stereocomplexed polycarbonates are mostly focused in the literature, the detailed investigations of their structures and the stacking interactions between the *R*- and *S*- chain are rather limited. Very few crystal structures of carbonate polymers except for the PLC reported by Coates et al. [16] were solved through X-ray diffractions since most of them always show broad diffraction peaks. Whereas, elucidating the interactions between opposite configuration polymers in stereocomplex at atomic level is critical to design novel CO_2 copolymers with enhanced performance for their potential applications.

Solid-state NMR is a powerful tool to probe the structure configurations and dynamic processes for both inorganic materials

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and organic polymers [17–21]. For example, the local structural information on the monomeric unit connectivities and stereochemical conformations of polymers was elucidated through the combination of ^{1}H and ^{13}C NMR experiments and quantum-chemical calculations of polymers [22–24]. Local dynamics of different groups in polymers can also be explored by ^{13}C spin–lattice relaxation times (T_1) [25]. Moreover, the spatial proximities or bond connectivities are manifest by two-dimensional (2D) NMR techniques through dipolar-coupling interactions between spinning pairs. Specific chain packing information is accessible via the distance-sensitive dipolar interactions between the specific proton and carbon positions at building blocks in close proximity using 2D NMR techniques such as ^{1}H–^{13}C heteronuclear correlation (HETCOR) solid-state NMR [26,27]. Herein, the interactions between *R*- and *S*- chain, and the related stereochemistry in a typical stereocomplexed polycarbonates, PCXC, are investigated in details utilizing one-dimensional ^{13}C CP/MAS, ^{1}H DUMBO MAS NMR, $^{13}C/^{1}H$ spin–lattice relaxation times (T_1), as well as 2D ^{1}H–^{13}C HETCOR NMR in a combination with the DFT calculations. It is found that the ordered interlock interactions between *R*- and *S*- chain result in the significant conformation changes bearing distinct NMR signal splitting of the backbone methine groups, and further reducing the mobilities of the carbon groups in the stereocomplexed PCXC.

2. Experimental

2.1. Sample preparation

PCXCs were prepared according to a procedure previously reported by Lu's group [28]. Briefly, 4,4-dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (30 mmol, 1000 equiv), racemic dinuclear Co(III) complex as catalyst (0.030 mmol, 1 equiv), and cocatalyst bis(triphenylphosphine)iminium 2,4-dinitrophenoxide (0.030 mmol, 1 equiv) were dissolved in toluene, and then transferred to a pre-dried 20 mL autoclave with magnetic stirring in an argon atmosphere. After CO_2 was introduced, the reaction mixture was stirred at 25 °C for 2 h. After reaction, the crude polymer was dissolved in a 10 mL $CHCl_3$/MeOH (5/1, v/v) mixture with 0.5% HCl solution and precipitated from methanol. This process was repeated 3–5 times to completely remove the catalyst, and white polymer was obtained after vacuum drying.

2.2. Solid-state NMR characterizations

All solid-state MAS NMR experiments were performed on Agilent DD2-500 MHz spectrometer with ^{1}H and ^{13}C resonance frequencies of 499.8 and 125.6 MHz, respectively, using a 4 mm MAS NMR probe and a spinning rate of 11–14 kHz. ^{1}H–^{13}C CP/MAS NMR spectra were recorded with a contact time (ct) of 3 ms, and 400–600 scans were accumulated with a 4 s recycle delay. ^{1}H DUMBO NMR with windowless homo-nuclear decoupling detection [29] was carried out to reduce the homo-nuclear dipolar interaction and achieve high-resolution ^{1}H MAS NMR spectra under a spinning rate of 10 kHz and a 5 s recycle delay. ^{13}C and ^{1}H spin–lattice relaxation times (T_1) were measured by a saturation recovery involved CP MAS-based pulse sequence [30]. The 2D ^{1}H–^{13}C LG HETCOR experiments [31] were conducted at a magic-angle spinning (MAS) frequency of 15.0 kHz, a recycle delay of 2 s, ct = 20 μs, 1 ms and 3 ms, and 160–200 scans for a total of 64 t_1 increments. High-power ^{1}H SPINAL-64 decoupling was used during ^{13}C acquisition.

2.3. Models and computational methods

All DFT calculations were performed by Gaussian09 package [32] unless otherwise specified. As the strict planarity of the carbonate groups, two conformations (*cis*- and *trans*-) may exist for the arrangement of methoxyl-terminated model dimers of PCXC(R)/PCXC(S) (Scheme 1). The remaining variables are the torsion angles around the C2–O1 bonds, which is directly reflected by dihedral $\theta 1$ (Scheme 1), and the relative energies of dimers at varied dihedral $\theta 1$were analyzed. Even though other dihedrals along with the backbone atoms are considered, there is no intrinsic difference as the configuration of 7-membered ring is relatively fixed.

The conformational energy calculations were performed by the B97D functional [33] with 6-31G(d) basis set [34]. For each $\theta 1$, we only fixed $\theta 1$, and the dimers were optimized to the most stable geometric structures, and then the energies were calculated. The models of isolated methoxyl-terminated PCXC(R)/PCXC(S) chains with eight monomers were also built according to above optimized configurations of the most stable dimers. The chains were also optimized using the same method as used in analysis of dimers. The optimized structures and relative energies are shown in Fig. S1. ^{13}C NMR chemical shifts of above optimized dimers were calculated by GIAO method at the B3LYP/6-311G(d,p) level [35–37]. To validate the chemical shift calculations, we chose three model carbonates containing CH groups: cyclohexyl methyl carbonate (^{13}C δ_{CH}: 75.98 ppm), 1-(cyclopropyl)ethyl methyl carbonate(^{13}C δ_{CH}: 79.56 ppm), methyl 1-methylethyl carbonate(^{13}C δ_{CH}: 71.92 ppm) [38]. The ^{13}C NMR of CH groups in these model carbonates were also calculated after optimization at B3LYP/6-311G(d,p) level. All the calculated ^{13}C chemical shifts were referenced to tetramethylsilane (TMS) using the same calculation method. A linear regression equation between the calculated and experimental chemical shifts of these model carbonates can be derived (Table S1) [39,40]. The calculated ^{13}C chemical shifts of CH in dimers were corrected with the linear regression equation (Table S1).

3. Results and discussion

^{13}C CP/MAS NMR spectra of a series of PCXCs were previously reported by our group [28] but without detailed analysis. Herein they were partially adapted and shown in Fig. 1. The lines of atactic, enantiopure isotactic PCXCs (Fig. 1(1)–(3)) show the same features, while the signal of methine (CH) groups at 77.6 ppm is split into two peaks at 74.0 and 80.0 ppm for the stereocomplexed PCXC (Fig. 1(4)). At the same time, there is also about 1 ppm upfield shift of C_d (Fig. 1(4)). Because of the strong ^{1}H–^{1}H dipolar interactions the normal one-pulse ^{1}H MAS NMR spectra of PCXC samples have only a broad overlapped signal (not shown here). ^{1}H DUMBO MAS NMR spectra with significantly enhanced spectral resolution due to the reduction of the homo-nuclear dipolar interaction are also shown in Fig. 1. The signal at 1.3 ppm is attributed to CH_3, while the signals near 3.9 and 5.1 ppm are attributed to CH_2 and CH groups, respectively. However, the peak of CH near 5.1 ppm is also split into two peaks at 4.8 and 5.4 ppm, respectively, in the stereocomplexed PCXC (Fig. 1(4′)). ^{1}H spin-lattice relaxation time (T_1) measurements with local mobility information of specific group were carried out to follow the chain–chain interactions (Table 1). The results demonstrate that there is significant enhancement of ^{1}H T_1 relaxation times from the amorphous, enantiopure to the stereocomplexed PCXC. More specific information derived from our previous ^{13}C T_1 relaxation time study of C, C=O, CH, CH_2 and CH_3 groups indicates that obvious increase of relaxation times up to 4 to 5 fold is observed for the carbon groups such as CO, CH and CH_2 at/near the backbone of stereocomplexed PCXC chains compared to the amorphous PCXCs [28]. All these results indicate that there are significant changes of the local structures as well as the packing models of *R*- and *S*- chain when the stereocomplexed PCXC is formed. At the same time, very close packing between the *R*- and *S*- chain in the stereocomplexed PCXC significantly reduces the mobilities of backbone groups.

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