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One-pot synthesis of crystalline polycarbonate-*block*-polyesters†

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We herein describe a simple and efficient one-pot synthesis approach to prepare crystalline polycarbonate–polyester diblock copolymers by copolymerizing tetrachlorophthalic anhydride, CO_2, and ethylene oxide using a metal-free catalyst. The block copolymers possess a melting point as high as 169 °C and two distinct glass transition temperatures. It is also possible to control the length and composition of the copolymers, thereby customizing their crystallinity and physical performance.

Crystallization can endow polymers with attractive chemical and physical properties.[1] As a typical example, naturally derived polysaccharides (*e.g.*, chitin, cellulose) are ubiquitous and play an important role in human history.[2,3] Moreover, synthetic crystalline polymers have been flourishing since the last century, giving rise to various polymeric materials.[4–9] Compared to amorphous polymers without crystallinity, crystalline polymers share higher mechanical properties, improved thermal and chemical stabilities, and better processing performances, endowing them with broader application potentials.[10,11]

Currently, there are several well-studied and widely applied synthetic crystalline polymers, including polyolefins,[12] polyesters,[13] polyamides,[14] and polyether ether ketones.[15] However, polycarbonate polymers, which have several carbonate units in the polymer backbone, face high challenges in achieving crystallization. This difficulty is particularly pronounced in the polycarbonate polymers derived from carbon dioxide, as their irregular microstructure hinders crystallization. From our knowledge, semi-crystalline CO_2-based polycarbonates can only be obtained using specific asymmetric metallic catalysts with chiral epoxide monomers, which significantly increases the production costs in industrial settings.[16–20] Whereas these polymers not only facilitate carbon reduction through the utilization of carbon dioxide but also exhibit biodegradability due to the characteristics of the carbonate units,[21,22] the lack of crystallinity demands further improvements in the physicochemical properties.

Similar to the structure of polycarbonates, various polyesters exhibit good crystallinity, such as poly(ethylene terephthalate) (PET) and poly(lactic acid) (PLA).[12,23] The synthesis of polyesters and polycarbonates involves similar raw materials, which can be derived from acidic molecules and alcohol derivatives (*e.g.*, ethylene oxide).[24–27] Moreover, they can be prepared with identical catalytic systems *via* an anionic polymerization mechanism. Therefore, if the raw materials for polyesters and polycarbonates are integrated into a one-pot, it is possible to synthesize polycarbonate–polyester copolymers. More importantly, if there is a significant difference in the reactivity between the carbonate and ester components, we may afford a copolymer with a diblock structure. In this case, the long chains of the polyester are expected to impart crystallinity to the material,[28–30] while the carbonate is anticipated to guarantee high mechanical strength and stability.

Following this hypothesis, we herein select carbon dioxide (CO_2), ethylene oxide (EO), and tetrachlorophthalic anhydride (TCPA) as the reaction system to prepare a polycarbonate-*block*-polyester, where triethylborane (TEB) and tetrabutylammonium chloride (TBACl) serve as a metal-free Lewis acid–base pair catalyst. With this method, one-pot synthesis of crystalline diblock copolymers is fulfilled (Fig. 1a). The polymers possess a melting point (T_m) as high as 169 °C and two distinct glass transition temperatures (T_g). By screening the experimental parameters including the reaction temperature, duration, and catalyst, we can readily control the molecular weight and composition of the copolymer, thereby customizing the polymer crystallinity and mechanical performance.

The experiments are conducted using a one-pot method by dissolving all monomers and catalysts in the solvent dioxane and

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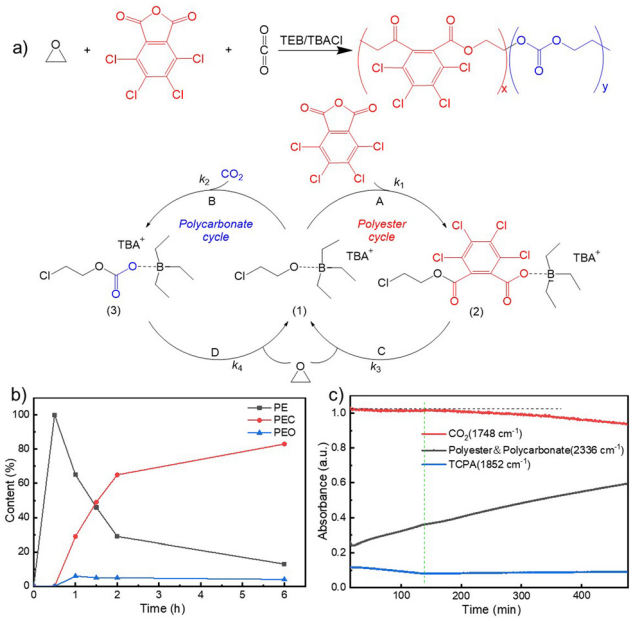

Fig. 1 (a) Plausible reaction mechanism of the copolymerization. (b) Polymer composition at different reaction times. (c) *In situ* infrared spectroscopy shows the consumption of anhydride monomers (1852 cm^{-1}), the incorporation of ester and carbonate bonds into continuously growing polymer chains (1748 cm^{-1}), and the consumption of carbon dioxide (2336 cm^{-1}). Note: The stretching of ester bonds in the obtained polymer overlaps with the stretching of carbonate bonds.

conducting the reaction under high temperature and pressure conditions. As expected, the polymerization of carbon dioxide (CO_2), ethylene oxide (EO), and tetrachlorophthalic anhydride (TCPA) primarily involves two catalytic cycles (Fig. 1a), which form a polyester and a polycarbonate, respectively. In the early stages of the reaction, triethylborane (TEB) and TBA^+ jointly stabilize the alkoxide anion active terminal (1), which was initially generated by the ring-opening of ethylene oxide. Then, TCPA and CO_2 compete to insert into the alkoxide end, generating carboxylate (2) and carbonate (3) intermediates, respectively. Since neither CO_2 nor TCPA can realize homopolymerization or copolymerization with each other, EO re-inserts into the carboxylate or carbonate ends, regenerating the alkoxide active species. According to the literature,[31–34] the insertion rate of TCPA or CO_2 into the alkoxide anion active terminal is faster than that of epoxide; thus, the polyester and polycarbonate are preferentially formed over polyether in this system. The polymer chain grows through repeated cycles of this polymerization. If the insertion rate of the anhydride (k_1) is much higher than the insertion rate of CO_2 (k_2), only polyester will form in the presence of anhydride, and CO_2 is only inserted to form the polycarbonate after the full conversion of all the anhydride. In other words, the reactant with much lower reactivity can only take part in the reaction after the total consumption of the more reactive chemicals. From this point, it is highly plausible to produce a product with a block structure.

To verify this hypothesis, we first studied the ^1H NMR and GPC test results of the reaction at different reaction time points to explore the progress of the copolymerization reaction. By observing the ester/carbonate unit content as well as the molecular weight of the products, we aimed to obtain chain growth information during the copolymerization (Fig. 1b and S1, S2, Table S1, ESI†). In the early stages of the reaction ($\leq$0.5 h), only ester units form, indicating that only TCPA reacts with EO initially. Later, carbonate units begin to form and no signal peaks of TCPA-EO-CO_2 linking segments are observed. This phenomenon is in good accordance with our hypothesis, where the rate of polyester formation is much faster ($k_1 \gg k_2$). In other words, the polycarbonate segments begin to grow only after all TCPA has been consumed. As the reaction continues, the polycarbonate segments continue to grow, the PEC signal peaks increase and the back-biting impurity of the PEC chain segment (ethylene carbonate) also appears.

To clarify the structure of the copolymer by excluding the possibility of a polymer mixture, DOSY NMR analysis was conducted. By measuring the diffusion coefficients of molecules, this measurement is particularly useful for distinguishing a mixture of two or three components with different self-diffusion factors. As shown in Fig. S3 (ESI†), the DOSY spectra revealed only a single signal with a low diffusion coefficient, indicating that the product is a copolymer instead of a blend of two polymers. In other words, the polycarbonate chain is initiated by the polyester instead of the small molecules.

To further prove that the product is a diblock copolymer, we studied the copolymerization kinetics using *in situ* infrared spectroscopy (Fig. 1c and Fig. S4, ESI†). All the reaction conditions and feed ratios were similar to those in Table S1 (ESI†), except for that the amount of CO_2 was fixed during the reaction. Interestingly, the *in situ* infrared results show that only TCPA is consumed in the early stages of the reaction, and the CO_2 content hardly changes, indicating that the polymerization occurs only with anhydride. After the full conversion of TCPA,

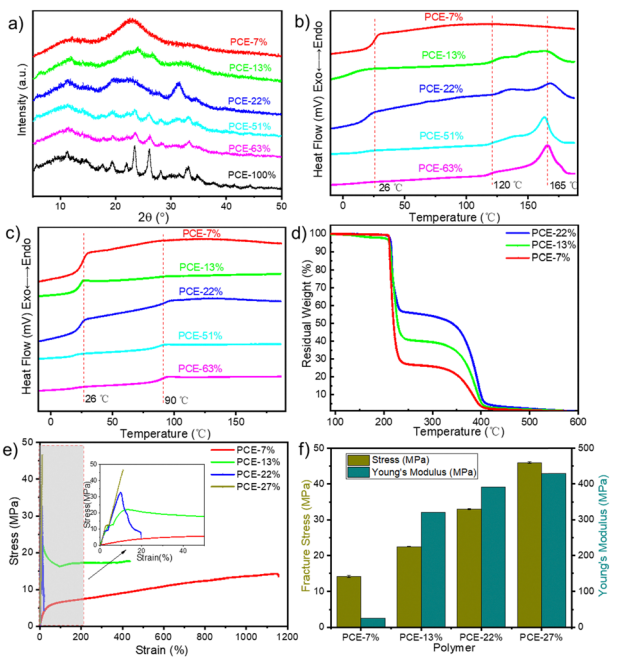

Fig. 2 Physical properties of PCE polymers with different chemical compositions. (a) XRD results; (b) and (c) first and second heating curves; (d) TGA results; (e) and (f) uniaxial tensile curves and mechanical parameters.

CO_2 begins to be consumed. As the reaction time extends, the polycarbonate content gradually increases. From the evidence above, it is safe to conclude the block structure of the polymers.

To better control the composition and molecular weight of the polymer, we further screened the effects of reaction conditions. The reaction temperature, initiator type and amount, and the catalyst acid–base component ratio are systematically investigated during the polymerization (Table 1 and Table S2, ESI†). As shown in entries 1–5, the rise in the reaction temperature from 50 °C to 70 °C led to a gradual increase in the conversion rate of EO. Moreover, the TOF value also increased from 60 h^{-1} to 247 h^{-1}, indicating that the copolymerization rate increases with temperature. However, higher temperatures make polycarbonate (PEC) more prone to forming the thermodynamically stable ethylene carbonate (EC) as a back-biting product of the polymer chain active terminal. To ensure high selectivity and reaction rate, we selected the reaction temperature of 60 °C for subsequent experiments.

Apart from temperature, the amount of catalyst is another important factor influencing the copolymerization reaction, which was investigated as follows. When the TEB/TBACl ratio was increased from 1 : 1 to 5 : 1 (Table 1, entries 6–11), the TOF of the copolymerization reaction increased. Interestingly, the amount of cyclic carbonate decreased with increasing TEB since the coordination between TEB and the electron-rich polymer terminal can effectively inhibit polymer chain back-biting. However, the rise in the TEB amount greatly raises industrial production costs and increases the polyester content. Since polyester in the polymer affects its degradation properties, we aim to minimize the formation of PEO and reduce by-products. Therefore, EO/TCPA/TEB/TBACl = 4000/100/4/1 is chosen as the optimal ratio for the reaction. Moreover, the co-reduction of TEB and TBACl (Table 1, entry 12) led to a polymer similar in composition to that of entry 2, yet it required a three times longer reaction time. Moreover, the reaction was performed by varying the contents of bis(triphenylphosphine)iminium chloride (PPNCl) and TBACl as Lewis bases under similar reaction conditions (entries 13 and 14). WhereasPPNCl exhibited stronger catalytic activity with nearly double the TOF value, it also led to a significant increase in the polyester content of the product, affecting its degradation properties. Therefore, TBACl was selected as the Lewis base for subsequent experiments. Overall, by comprehensively adjusting the reaction temperature, catalyst dosage, and reaction time, we can effectively control the composition and molecular weight of the product to meet the needs for different applications.

After synthesizing polymers with different polyester contents, we proceeded to study their physical properties. In the first place, the crystallization properties of the copolymers were investigated by the X-ray diffraction (XRD) test. For simplification, the copolymers are denoted as PCE-*x*, where C and E stand for carbonate and ester, and x represents the molar content of polyester in the copolymer. In the first place, pure polyester (PCE-100%) displayed multiple sharp diffraction peaks, while almost no diffraction peaks were observed in the PCE-7% copolymer, revealing that the crystallization ability of the PCE terpolymer is mainly provided by the polyester segments. With the decrease in polyester content in the copolymer, the crystallization ability becomes increasingly insignificant until crystallization is no longer possible. In addition, the multiple diffraction peaks in the XRD results also indicate the presence of different crystal forms in the polymer.

To further verify the crystalline performance, we studied the thermal behavior of the products using a differential scanning calorimeter (DSC). As shown in Fig. 2b, a distinct melting peak was observed during the first heating cycle of the DSC, with the polymer's melting temperature (T_m) reaching as high as 169 °C. Moreover, as the polyester content in the polymer increases, the melting peaks observed in the DSC become sharper, indicating that a higher polyester content promotes crystallization in the polymer. In addition, two glass transition temperatures (T_g) are observed: the lower one at 23 °C corresponds to the T_g of polycarbonate segments, and the higher one at 120 °C is attributed to the polyester segments. This suggests that the polyester segments in the polymer are in a mixed state of crystalline and amorphous regions, emphasizing again the block structure. Interestingly, only the glass transition temperature was observed for the PCE copolymer during the second heating cycle, and no melting peak disappeared, indicating the poor

Table 1 Experimental results of synthesizing the EO/TCPA/CO_2 terpolymer under different reaction conditions[a]

Entry	EO/TCPA/TEB/TBACl (molar ratio)	T (°C)	t (h)	TOF (h^{-1})[b]	PE/PEC/PEO (mol%)	CC (mol%)	M_n (kg mol^{-1})/PDI[c]	EO Conv. (%)[d]
1	4000 : 100 : 4 : 1	50	6	60	25/71/4	1	21.9/1.21	9
2	4000 : 100 : 4 : 1	55	6	80	20/75/6	2	28.2/1.13	12
3	4000 : 100 : 4 : 1	60	6	127	13/83/4	2	41.8/1.15	19
4	4000 : 100 : 4 : 1	65	6	187	11/84/5	3	44.9/1.14	28
5	4000 : 100 : 4 : 1	70	6	247	9/83/8	4	60.5/1.22	37
6	4000 : 100 : 1 : 1	60	6	40	49/49/2	21	10.2/1.24	6
7	4000 : 100 : 1.5 : 1	60	6	53	38/60/2	12	18.4/1.23	8
8	4000 : 100 : 2 : 1	60	6	67	25/73/2	8	20.6/1.23	10
9	4000 : 100 : 3 : 1	60	6	93	17/79/3	4	29.1/1.21	14
10	4000 : 100 : 4 : 1	60	6	120	14/81/5	2	34.5/1.22	18
11	4000 : 100 : 5 : 1	60	6	133	13/81/6	2	35.8/1.19	20
12	4000 : 100 : 2 : 0.5	60	18	62	22/75/3	7	52.1/1.28	14
13[e]	4000 : 100 : 1 : 1	60	20	6	18/80/2	28	19.9/1.30	14
14[e]	4000 : 100 : 4 : 1	60	20	6	7/70/23	1	56.1/1.22	33

[a] All the polymerizations were carried out with a fixed monomer feed ratio (17.6 g EO + 2.85 g TCPA) in autoclaves with 20 g of dry dioxane. [b] TOF (h^{-1}) = mol (EO consumed)/[t × mol (base)]. [c] Determined by GPC in chloroform. [d] Calculated by ^{1}H NMR. [e] PPNCl was used instead of TBACl.

crystallization ability of the copolymer. Similar findings were reported previously,[30] where a semicrystalline polymer required more than 7 days of isothermal crystallization to recrystallize. Correspondingly, the glass transition temperature of the polyester during the second heating process is somehow lower than the first cycle, which can be attributed to the disruption of crystalline domains (Fig. 2c). The presence of the crystalline regions makes it more difficult for the amorphous polyester chains to move, thereby increasing their glass transition temperature. In other words, the presence of crystallization enhances the thermal properties of the PCE terpolymer to a certain extent.

Apart from the DSC measurements, a thermogravimetry analysis (TGA) experiment was also carried out to investigate the thermal properties. As depicted in Fig. 2d, the polymer samples show two distinct steps. By comparing the composition of the copolymers, it was observed that the first step corresponds to the decomposition of the PEC segments, and the second one corresponds to the decomposition of the polyester. The results indicate that the polyester content does not affect the thermal decomposition temperature of the product, since the T_{d5} values of the three samples with different polyester contents were all around 210 °C (Fig. S5, ESI†). This further confirms that the polymers possess block structures since the polyester content does not affect the thermal stability of the PEC segment.

In addition, we evaluated the mechanical properties of the polymers (Fig. 2e and f). Due to the poor crystallization ability of the terpolymer, it was not possible to obtain uniformly distributed crystalline polymer samples by hot pressing, so we only tested the mechanical properties of the amorphous samples. With the rise in polyester content from 7 mol% to 27 mol%, the tensile strength of the copolymer increased from 14 MPa to 47 MPa, while the elongation at break decreased from 1155% to 10%. When the polyester content is higher than 27 mol%, the material becomes too brittle to undergo the tensile test. Similarly, Young's modulus of polymers demonstrated a positive correlation with the polyester content. Therefore, we can fine-tune its tensile strength and elongation at break to meet the needs for practical applications by adjusting the polymer composition.

In summary, we have developed a one-pot approach to prepare a crystalline polycarbonate–polyester diblock copolymer with CO_2/TCPA/EO using a metal-free Lewis acid–base pair. The copolymer demonstrates a pronounced crystallization performance with a high T_m and two distinct T_g. Upon adjusting the polyester content by varying the experimental conditions, we can readily obtain products with different crystallinity degrees and mechanical properties. Due to its unique crystallization behavior *via* such a simple approach, it has broad potential applications in fields such as battery binders. Furthermore, more crystalline polymers are foreseeable *via* such an approach in the future.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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