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PAPER

Semi-crystalline Terpolymers with Varying Chain Sequences Structure Derived from CO_2, Cyclohexene Oxide and ε-Caprolactone: One-step Synthesis Catalyzed by Tri-zinc Complexes

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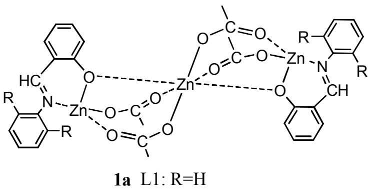
The novel semi-crystalline terpolymers with varying chain sequences structure derived from cyclohexene oxide (CHO), CO_2 and ε-caprolactone (CL) is firstly synthesized and reported. The terpolymerization is catalyzed by Schiff base tri-zinc complexes via a one-step route. The tri-zinc complexes also exhibit a very highly catalytic activity for the homopolymerization of ε-caprolactone in the absence of CHO. A series of terpolymers with varying contents of crystalline segment are produced by adjusting the feedstock ratio of CHO/ε-CL. The reactivity of different monomers were investigated by experimental methodology. The results indicate that ε-CL is much more active than CHO in this terpolymerization system. Therefore, the incorporation of ε-CL can dramatically improve the TONs of terpolymer containing ε-CL moieties. Moreover, the thermal properties of resulting terpolymers were also studied by DSC and TGA. Finally, the polymerization mechanism of this ternary system is extensively discussed based on experiment phenomena. To the best of our knowledge, this is the report on the novel catalysts to be capable of synthesizing polycarbonates, polyesters and poly (carbonate-ester) via one-step polymerization.

Introduction

Over the last decade, world-wide research effort has developed a variety of highly active catalysts for synthesizing poly (propylene carbonate) (PPC) and poly (cyclohexene carbonate) (PCHC), utilizing carbon dioxide and epoxides.[1-12] CO_2 copolymers are biodegradable, highly transparent, UV stable, and have a high Young's modulus[13,14], showing great potential as "green chemistry" plastics. However, polycarbonates produced from CO_2 cannot match the properties of conventional polycarbonate materials, for example, low glass transition temperature of PPC and brittleness of PCHC. Moreover, the production cost of CO_2 copolymers needs to be improved to allow widespread impact. First of all, catalysts for the copolymerization are essential to develop both the production efficiency and the physical/chemical properties of polycarbonates. Advanced improvements towards catalyst activity and selectivity, as well as copolymer stereo-regularity, will offer tremendous prospect for the popularization of CO_2 copolymers. Latest researches have opened some routes to fabricate semi-crystalline CO_2 copolymers via regulating the ring-opening step using stereo- and regioselective catalysts.[15-20] On the other hand, it is feasible to bring in other compounds for the polymerization reaction of CO_2 and epoxides, thus to adjust the physical properties. Similar work has been well documented via introducing other epoxides, aliphatic/alicyclic anhydrides, cyclic diesters or lactones.[11,21-30] The main challenge is how to coordinate the various reactivity of the chosen chemicals during the ter- or multi-polymerization with CO_2. Thus, the first priority is to develop appropriate multifunctional catalysts, capable of getting rid of catalysts poisoning and then controlling the composition of the resultant polymers.

Recently, we reported a highly efficient process for the copolymerization of CO_2 and cyclohexene oxide (CHO) catalyzed by low-cost and easily-prepared tri-metallic zinc-based complexes (**Scheme 1**)[31]. Inspired by the use of similar zinc-based catalyst systems for synthesizing polylactide, poly (ε-caprolactone) (PCL) and their copolymers[32-36], we tried to bring in crystalline chain segments onto the backbone of polycarbonates using our Zn complexes. PCL, a polymer with high crystallinity (can reach 69%)[37], has been widely used as biomedical materials for a long time. Over the past two decades, however, PCL has drawn considerable attention as potential replacements for conventional petro-chemically derived polymers. Owing to the biodegradable and biocompatible characteristic of PCL, PCL is also regarded as environmentally friendly materials.[38,39] Herein, we firstly conduct the terpolymerization of CO_2, CHO and ε-caprolactone (ε-CL)



1a L1: R=H
1b L2: R= *i*Pr

Scheme 1 Structures of catalysts **1a~b.**

employing our tri-zinc catalysts in one-step method. By adjusting the feedstock ratio of CHO/ε-CL, a series of terpolymers with diverse degrees of crystallinity and molecular weights are produced. These semi-crystalline terpolymers exhibit better flexibility and lower melting temperatures than that of pure PCHC, which would benefit mechanical processes.

Experimental Section

Materials and Measurements.

All manipulations were operated without an atmosphere of nitrogen unless otherwise stated. 2, 6-Diisopropylaniline, ε-caprolactone and CaH_2 were obtained from Aladdin Reagent. Methanol, ethanol, dichloromethane, 88% formic acid, salicylaldehyde, phenylamine and zinc acetate dihydrate were purchased through commercial sources. Cyclohexene oxide (>95.0%, industrial reagent) was freshly distilled from CaH_2 after reflux for 40h under dry nitrogen gas prior to use. ε-Caprolactone was dried with CaH_2 for 24 h at room temperature and then distilled under reduced pressure. The other reagents listed above were used without further purification. Bone dry carbon dioxide (>99.99%, Shanghai Zhenxingaisi Gases) was supplied in a high pressure cylinder equipped with a relief valve and copper pipe.

^1H NMR spectra were recorded on a Bruker DRX-500 MHz NMR spectrometer. Thermogravimetric analysis (TGA) was conducted on Perkin Elmer Pyris Diamond thermogravimertic /differential thermol analyzer (TG/DTA). T_m was acquired via DTA curves. Molecular weight determinations were carried out using a Waters gel permeation chromatography (GPC) system with chloroform as eluent. The GPC system was calibrated by a series of polystyrene standards with polydispersity of 1.02. The glass transition temperatures (T_g), crystallization temperatures (T_c) and melting points (T_m) were measured by a differential scanning calorimeter (DSC, Netzsch Model 204). T_g and T_m of the samples were determined from the second heating run. T_c was determined from the cooling run. In situ IR measurements were performed using a Mettler-Toledo ReactIR 45 system equipped with a MCT detector and DiCOMP probe.

Catalysts Synthesis.

These two Schiff base ligands were prepared via the condensation reaction of salicylaldehydes and aromatic amines, referring to the procedures that have been reported for analogous compounds.[40] Subsequently, 5.1 mmol of the obtained ligands were added into a transparent solution of $Zn(OAc)_2•2H_2O$ (1.10 g, 5.1 mmol) in methanol (20 mL). [41] The mixture was then stirred for 1h at ambient temperature, giving precipitates appearing pale yellow. The product was isolated by vacuum filtration and washed twice with MeOH. The refined complexes were dried at 80 °C under vacuum for 24 h. The construction and purity of catalysts was confirmed by ^1H NMR and elemental analysis as we have done before.

General Procedure for Terpolymerization of CO_2, CHO and ε-CL and synthesis of PCL.

All terpolymerization manipulations were carried out in a 500 mL stainless steel autoclave equipped with a mechanical stirrer. The typical experiment, a defined amount of catalyst ([CHO+ε-CL]:[cat]=1000:1) was introduced into the autoclave followed by sealing up, pumping to vacuum and heating to 80 °C. Having been dried for 8 h, allotted quantities of distilled ε-CL and CHO were added into the reactor. The reactor was heated up to 80 °C, pressurized to 5.0 MPa via CO_2 cylinder, and then stirred for 20 h. After the assigned time, the autoclave was cooled to ambient temperature and vented. The reactor was opened and a small amount of crude product was immediately taken as test sample for ^1H NMR spectrum. Methylene chloride was used to dissolve the viscous mixture consisting of polymers, by-product, catalyst and unreacted monomer. The target product was purified by precipitation from icy ethanol. The refined polymer was dried in vacuum for 24 h and subsequently weighed to calculate productivity. The product without any workup was analyzed by ^1H NMR, where the quantities of PCHC, PCL, cyclic CHC and PCHO were calculated by integrating the peaks of protons adjacent to δ=4.64, 4.08, 4.05 and 3.45 ppm in turn **(Fig. 1)**.

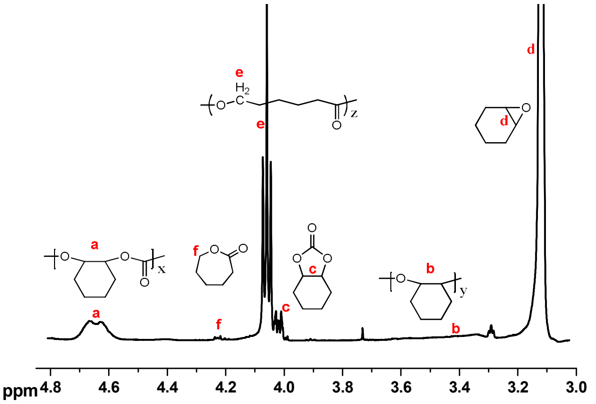
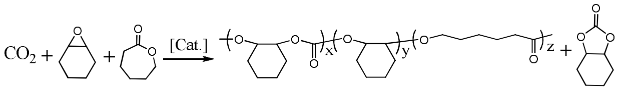


Fig. 1 Typical ^1H NMR ($CDCl_3$) spectrum of the crude product used for determination of polymer and byproduct contents. This sample was operated under the condition of 10% ε-CL feedstock, 80 °C, 5 MPa and 5 h. The methene peak (f) of ε-CL resides at 4.23 ppm.

The synthesis of PCL was operated in a 50 mL Schlenk flask under an atmosphere of nitrogen. Arranged amounts of catalyst and ε-CL ([ε-CL]:[cat]=1000:1) were injected into the dried flask, following pumping for vacuum and aerating nitrogen in turn for three times. The reactor was heating up to setting temperatures and held for 20 h. Afterwards, the equipment was cooled down and added enough dichloromethane to dissolve the crude product. The resulted solution was poured into icy ethanol for precipitating the polymer. Finally, the purified PCL was dried in vacuum for 24 h and later weighed to calculate the conversion of ε-CL.

Terpolymerization Monitored by *in suit* IR Spectroscopy

A customized 2 L stainless steel autoclave, available for the application of the ReactIR 45 system, was employed in the reaction. The catalyst was added into the reactor, followed by sealing up, pumping to vacuum, heating to the desired temperature and drying for 8 h. A single 256-scan background spectrum was collected, and then defined quantities of distilled ε-CL and CHO were added. The reactor was pressurized to 5.0 MPa of CO_2 as the IR spectrometer start to collect spectra. The *in suit* IR system was set up to collect one spectrum every 2 minutes.



Scheme 2 Terpolymerization of CO_2, CHO and ε-CL.

Theoretical Calculation of Charge Density.

The density functional theory calculations were carried out for all copolymerization monomers (ε-CL, CHO and CO_2). For geometry optimization and natural bond orbitals (NBO) analysis, the density function theory (DFT) method B3LYP [46,47] in combination with 6-311G(d, p) basis set was employed in the Gaussian 03 program [48]. The NBO charges for the oxygen atoms of all monomers were calculated.

Results and Discussion

Terpolymerization of CO_2, CHO and ε-caprolactone.

In the present study, we successfully accomplished the terpolymerization of CO_2, CHO and ε-caprolactone catalyzed by Schiff base tri-zinc complexes **1a~b** (**Scheme 1**), producing alicyclic carbonate-ester terpolymers (**Scheme 2**). The reaction was carried out in a bulk system. The products of this terpolymerization were found to be highly soluble in CHO and ε-CL, indicating that CHO and ε-CL serve as both monomers and reaction media. Firstly, the terpolymerization was undertaken under 5 MPa for 20 h at different temperatures ranging from 70 to 100 °C, as shown in **Table 1**. The percentage of each monomer incorporated into polymer chains as well as by-products (cyclic cyclohexene carbonate and poly cyclohexene oxide) was analyzed by ^{1}H NMR spectroscopy in $CDCl_3$. It was found that the optimal reaction temperature is 80 °C, considering selectivity of desired product, polymer composition and molecular weights. Broad molecular weight distributions in GPC traces of these five samples are observed. When calculating molecular weights of the terpolymers, the broad trace was divided into two parts and integrated respec-

Table 1 Terpolymerization of CO_2, CHO and ε-CL using catalyst **1b** at different temperatures [a]

Entry	Temp./°C	TON [b]	Selectivity/% [c]	Polymer Composition/% [d]			M_n/kg mol^{-1} [e]	M_w/M_n
				CHC	CL	CHO		
1	100	384	80	50.3	35.2	14.6	83.7 7.7	1.55 1.69
2	90	368	84	51.8	32.1	16.1	43.7 6.7	2.27 1.62
3	80	288	91	55.9	32.4	11.7	115.1 9.3	3.10 1.48
4 [f]	80	219	93	47.4	46.5	6.2	69.2 10.3	2.22 1.34
5	70	234	92	38.9	45.5	15.6	100.0 9.9	2.82 1.43

[a] All reactions were performed in mixture of [CHO]:[CL]:[Cat.]=900:100:1 (0.493 mmol Cat.) under 5MPa for 20h. [b] Mole of [CHO+CL] consumed per mole of [Cat.]. [c] Molar ratio of terpolymer and cyclic carbonate, calculated by ^{1}H NMR spectra of unrefined product (CDCl3, 500 MHz). [d] Molar ratio of CHC, CL and CHO units, calculated by ^{1}H NMR spectroscopy. [e] Determined by GPC, calibrated with polystyrene standards in $CHCl_3$. [f] Entry 4 was catalyzed by **1a**.

Table 2 Terpolymerization of CO_2, CHO and ε-CL using catalyst **1b** with varying feedstock ratio [a]

Entry	CHO:CL [b]	TON [c]	Selectivity/% [d]	Polymer Composition/% [e]			M_n /kg mol^{-1} [f]	M_w/M_n
				CHC	CL	CHO		
1	10:0	180	96	94.0	--	6.0	45.5	4.37
2	39:1	270	88	68.0	11.6	20.4	137.6 4.8	4.50 1.96
3	19:1	267	86	61.7	20.4	17.9	87.8 7.4	2.75 1.53
4 [f]	9:1	288	91	55.9	32.4	11.7	115.1 9.3	3.10 1.48
5	8:2	301	93	28.8	59.9	11.2	12.4	1.59
6	7:3	350	94	12.7	82.7	4.6	25.5	1.41
7	6:4	442	95	6.0	90.9	3.0	27.4	1.51
8 [g]	0:10				20%		5.9	1.90
9 [g, h]	0:10		Conversion		91%		22.9	1.79
10 [g, i]	0:10				99%		29.9	1.64

[a] All reactions were performed in mixture of [CHO+CL]:[Cat.]=1000:1 (0.493 mmol **1b**) under 80 °C, 5MPa for 20h. [b] Molar ratio of feeding [CHO] and [CL]. [c] Mole of [CHO+CL] consumed per mole of [Cat.]. [d] Molar ratio of polymer and cyclic carbonate, calculated by ^{1}H NMR spectra of unrefined product ($CDCl_3$, 500 MHz). [e] Molar ratio of CHC, CL and CHO units, calculated by ^{1}H NMR spectroscopy. [f] Determined by GPC, calibrated with polystyrene standards in $CHCl_3$. [g] Feedstock: 10 mL of ε-CL, [CL]:[Cat.]=1000:1. The conversion of CL was calculated by ^{1}H NMR spectra. [h] Entry 9 was operated at 100 °C. [i] Entry 10 was operated at 140 °C.

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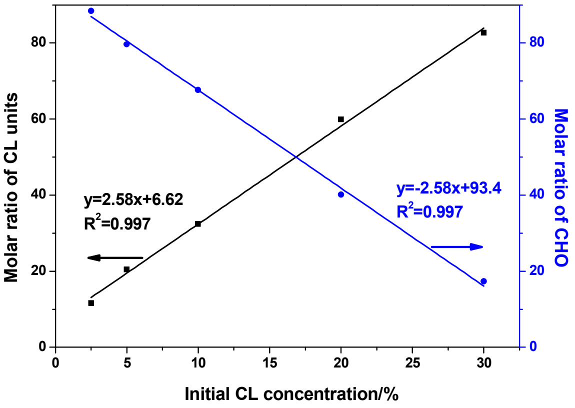

Fig. 2 Plot showing the linear fit to molar ratio of ε-CL/CHO vs initial concentration of ε-CL.

tively. Entry 4 shows that catalyst **1a** has a smaller TON in this ternary reaction system, mainly because the conversion of cyclohexene oxide catalyzed by **1a** is lower than that catalyzed by **1b.** This has been demonstrated by our previous copolymerization of CO_2 and CHO [31]; nevertheless, other performances such as selectivity, ether linkage content and polydispersity are better.

As shown in **Table 2**, a series of terpolymers with various contents of crystalline segment were produced by adjusting the feedstock ratio of CHO/ε-CL. Most importantly, it is especially interesting that our tri-zinc complexes are also capable of synthesizing PCL in the absence of CHO, although the monomer conversion is not very high. Elevating reaction temperatures can effectively increase the monomer conversion up to 99%. The zinc complexes reported in literature are generally not capable of producing polycarbonates, polyesters and their terpolymers in one-step synthesis.[30,42,43] Compared with entry **1**, the TON of entry **2** increases obviously from 180 to 270 with introducing ε-CL. This indicates that ε-CL is much more active than CHO, and thus facilitates this reaction. Also, the TONs increase gradually up to 442 with further increasing the percentage of ε-CL in the feed from 2.5% to 40%. Consequently, the molar proportions of CL units in polymers range from 11.6% to 90.9%. **Fig. 2** shows the linear relationship between the molar ratios of CL/CHO units in polymers with initial feeding concentration of ε-CL. The intersection point of two linear indicates that a polymer with 50% CL units can be obtained in case that the feed ratio of ε-CL is about 17%. Compared with the copolymerization of CO_2 and CHO, the addition of only 2.5% ε-CL favours the formation of cyclic carbonate and polyether. However, the selectivity of polycarbonate can be enhanced and the proportion of ether linkages can be decreased by increasing ε-CL loading. Although the similar work has just been disclosed by Williams group,[42] our catalyst can produce PCL in the absence of CHO. Moreover, both PCHC and PCL units were found to be produced under the CO_2 pressure of 5 MPa when using our catalyst.

Thermal Properties of Terpolymers.

DSC and TGA were employed to determine the glass transition temperatures (T_g), crystallization temperatures (T_c, peak-values of crystallization peaks), melting points (T_m) and decomposition temperatures ($T_{5\%}/T_{max}$) of as-synthesized terpolymers. All thermal parameters are summarized in **Table 3.** DSC thermograms of terpolymers with varying composition are shown in **Fig. 3**. All T_g and T_m values were acquired on the second heating run of DSC test. As anticipated, the thermal properties for the synthesized terpolymers are highly dependent on the composition

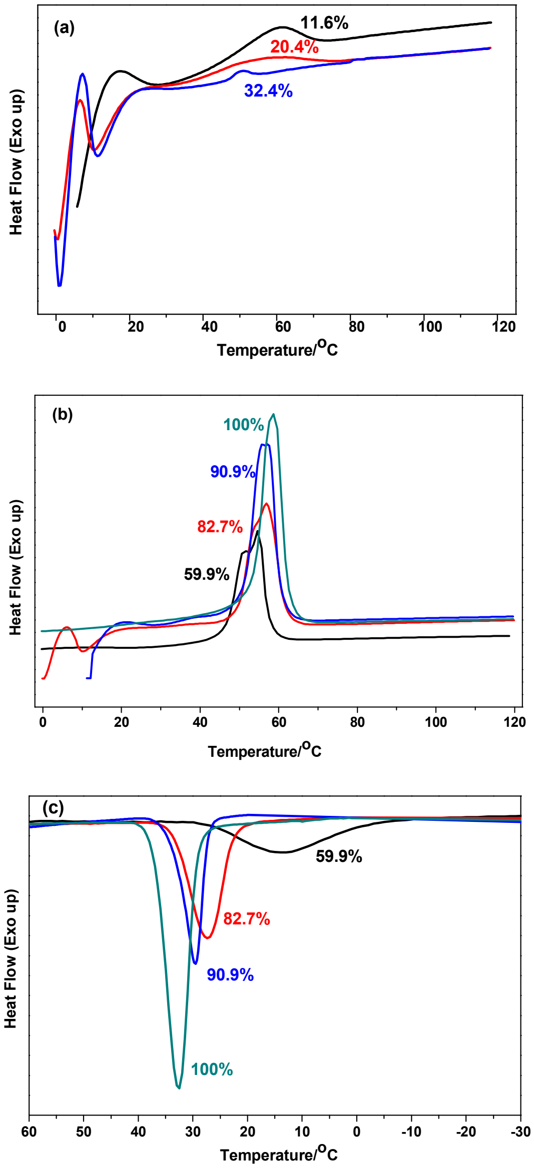

Fig. 3 DSC thermograms for the terpolymers with different contents of CL units: second heating run (10K/min) for (a) glass transition & (b) melting peaks; cooling run (-5K/min) for (c) recrystallization.

Table 3 Thermal properties of terpolymers with varying contents of CL unit [a]

CHO: CL [b]	CL unit (%) [c]	T_g/ T_m (°C)	$T_{5\%}$/ T_{max} (°C)
10:0	--	121.2/--	200.9/280.0
39:1	11.6	49.8/--	210.2/280.7
19:1	20.4	46.8/--	227.7/288.2
9:1	32.4	46.6/--	262.1/284.3
8:2	59.9	--/55.0	216.6/322.9
7:3	82.7	--/56.6	256.5/341.1
6:4	90.9	--/57.3	262.0/342.4
0:10	100	--/58.9	281.5/345.2

[a] T_g and T_m was detected by DSC measurement. $T_{5\%}$ and T_{max} were determined via TGA. [b] Molar ratio of feeding [CHO] and [CL]. [c] Molar contents of CL units in polymers.

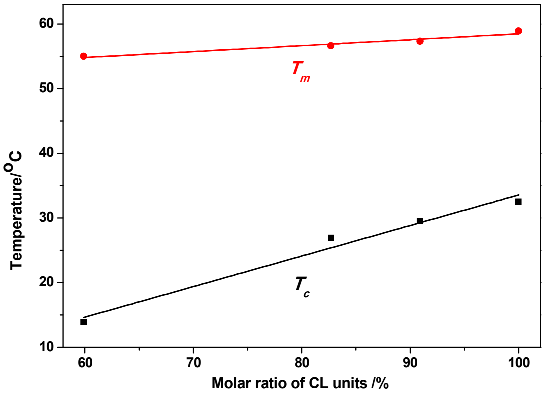

Fig. 4 Plots of the dependence of T_c (bottom), and T_m (top) of terpolymers on the molar ratio of CL units in terpolymers.

of different monomers incorporated into polymer backbone. The PCHC copolymer without CL units shows a T_g of 121.2 °C as expected because of the rigid nature of molecular chain of PCHC. Pure PCL exhibits a T_m of 58.9 °C that matches with the previous reported data.[39] The terpolymers consisting of little CL units (≤32.4%) have glass transition at about 46~50 °C ascribed to both the flexible nature of CL molecule and the amorphous PCHC segments. The T_g of terpolymers decreases slightly with increasing the content of flexible PCL moieties. Large amount of amorphous PCHC segments (≥67.6%) can prohibit the crystalline formation of PCL segments. However, the terpolymers exhibit the crystalline characteristics when CL moiety contents are higher than 60% as shown in **Fig. 3(c),** which shows melting points ranging from 55 to 59 °C. **Fig. 4** shows the linear dependence of T_c and T_m of terpolymers on the molar proportion of CL units within the terpolymers. It can be seen that both T_c and T_m increase with increasing the content of CL moiety. From **Table 3**, it is apparent that the $T_{5\%}$ and T_{max} of neat PCL are much higher than those of PCHC terpolymers. In this connection, the thermal stability of terpolymers is greatly improved by the incorporation of CL moieties into copolymers.

Investigation of Polymerization Mechanism.

In order to further make clear the polymerization process of CO_2, CHO and ε-CL in the presence of synthesized catalyst, the polymerization was carried in varying duration ranging from 5 to 40 h. The results are given in **Table 4**.

Fig. 1 shows the terpolymer structure that synthesized within 5 h. It is apparent that ε-CL was totally converted into terpolymer, demonstrating its highly reactivity. This also implies an unusual terpolymer formed with long sequence of CL units and less quantity of carbonate linkages. It has been reported that the carbonyl oxygen rather than ether oxygen initially coordinates with metal center at the living ends during the coordination polymerization of cyclic esters.[39,44,45] Compared with ε-CL, the relatively steric bulk effect may hinder the formation of Zn-O bond in the ring opening step of CHO. Another factor that influences on the formation of Zn-O bond is believed to be the negative charge densities of monomer oxygen atoms. Based on the natural bond orbitals (NBO) charges from density function theory (DFT) calculation, **Fig. 5** illustrates the negative charge densities of oxygen atoms for ε-CL (carbonyl: -0.546, ether: -0.559), CHO (-0.572) and CO_2 (-0.466). Although the density of negative charges for the ether oxygen of CHO is larger than that for the carbonyl oxygen of ε-CL, the rate-determining step for the copolymerization of CHO/CO_2 in this catalytic system is CO_2 insertion[31]. The NBO charge value of -0.466 for CO_2 can well explain its inherent inertness in this reaction. Another consideration is that due to electronic density around alkoxide bonds, the alkoxide provided by the ring-opening of a CHO monomer should bind to zinc more strongly than the alkoxide afforded from the ring-opening of caprolactone, thereby resulting in a slower polymerization process. However, besides monomer nature, the kinetic factors such as monomer concentration also play a crucial role in the competition of ring opening. When ε-CL monomer is consumed to some extent, CHO/CO_2 pair can competitively take the place of ε-CL to coordinate with metal center, leading to the carbonate linkages formation.

Table4 Terpolymerization of CO_2, CHO and ε-CL using catalyst **1b** via adjusting reaction times [a]

Entry	Time/h	TON [b]	Selectivity/% [c]	Polymer Composition/% [d]			M_n /kg mol^{-1} [e]	M_w/M_n
				CHC	CL	CHO		
1	5	165	93	27.6	62.2	10.2	7.1	1.37
2	20	288	91	59.9	32.4	11.7	115.1 9.3	3.10 1.48
3	40	572	87	66.7	20.7	12.7	234.3 7.9	2.97 1.96

[a] All reactions were performed in mixture of [CHO]:[CL]:[Cat.]=900:100:1 (0.493 mmol Cat.) under 80 °C, 5MPa. [b] Mole of [CHO+CL] consumed per mole of [Cat.]. [c] Molar ratio of polymer and cyclic carbonate, calculated by ^{1}H NMR spectra of unrefined product ($CDCl_3$, 500 MHz). [d] Molar ratio of PCHC, PCL and PCHO, calculated by ^{1}H NMR spectroscopy. [e] Determined by GPC, calibrated with polystyrene standards in $CHCl_3$.

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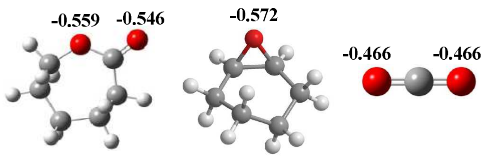

Fig. 5 DFT: B3LYP/6-311G (d, p) optimized geometries and NBO charges for ε-CL, CHO and CO_2 from left to right. (**O**: red, **C**: gray, **H**: white).

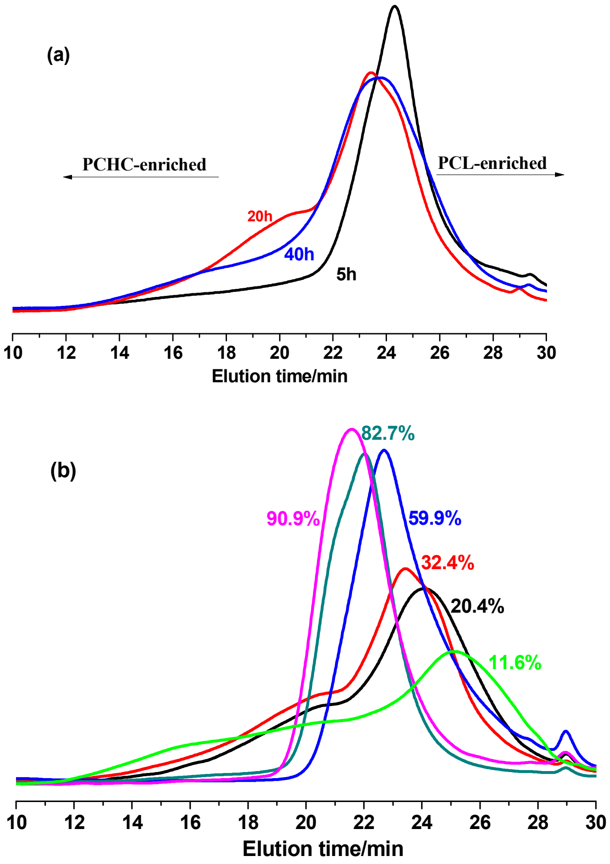

Fig. 6 GPC plots of terpolymers produced with (a) varying reaction times and (b) varying percentages of CL units.

Fig. 6 shows the broad molecular weight distributions of resulting terpolymers detected by GPC. **Fig. 6(a)** indicates that the polymers indeed keep on propagating under the circumstance that very little ε-CL monomer remained as determined by ^{1}H NMR analysis. This means that the insertion of cyclohexene carbonate unit is dominant in later reaction period, which is proved via ATR *in suit* IR shown in **Fig. 7(a)**. In this sense, we believe that the product derived from the terpolymerization should be a terpolymer consisting of both ester and carbonate linkages. On the other hand, the broad molecular weight distribution is presumably resulted from the big difference in the reactivity between CHO/CO_2 pair and ε-CL monomer, as well as the possible chain-transfer reaction, especially when extending reaction times. Based on the results of ^{1}H NMR, GPC and *in suit* IR measurements, the terpolymer with PCL-enriched sequence is firstly formed, and thereafter, the terpolymer with PCHC-enriched yielded when PCL is almost consumed. The ATR *in suit* IR results demonstrate well that ε-CL monomer polymerizes first and the polymerization carries out in an anionic coordination mechanism. **Fig. 7(b)** shows the molecular weights formed with varying CL contents. It can be also seen that the molecular weight increases with both increasing CL content and reaction time. The result indicates further the fact that CL monomer is much active compared to CHO/CO_2 pair. Besides, the broad distribution also reveals that a portion of polymer-chain end may deactivate in later reaction period. Thereby, a chain-transfer reaction of the propagating polymer chain end could possibly occur in the presence of cyclohexene oxide at elevated temperatures.[42,49] The reason that the chain-transfer reaction emerges in later period can be ascribed to the slower enchainment of CHO/CO_2 than that of ε-CL. Consequently, longer reaction time makes broader molecular weight distribution. On the basis of all experimental results above, a graphical reaction progress for the terpolymerization of CO_2, CHO and ε-CL is depicted in **Fig. 7(b)**. **Fig. 7(b)** describes the formation of PCL-enriched segment because of the monomer nature in early period of the reaction, and that of PCHC-enriched segment due to kinetic factors in later period.

Conclusions

In this work, a novel semi-crystalline terpolymer with two different chain sequences structure derived from cyclohexene oxide, CO_2 and ε-caprolactone is firstly synthesized and reported. The terpolymerization is catalyzed by Schiff base tri-zinc complexes via a one-step route. To our knowledge, they are the first catalysts to be capable of synthesizing the terpolymers containing polycarbonates, polyesters and poly (carbonate-ester) via one-step synthesis. ε-CL was proved to be much active than CHO in this ternary system and thus dramatically improved the TONs of catalyst **1b**. The decomposition temperatures of synthesized polymers dramatically increase by the introduction of CL units. The ring opening of ε-CL is much faster than the alternating insertion of CHO/CO_2 pair because of both steric and electronic effect. PCL-enriched segment forms in early period of the reaction, and PCHC-enriched segment yields in later period, leading to the broad molecular weight distribution.

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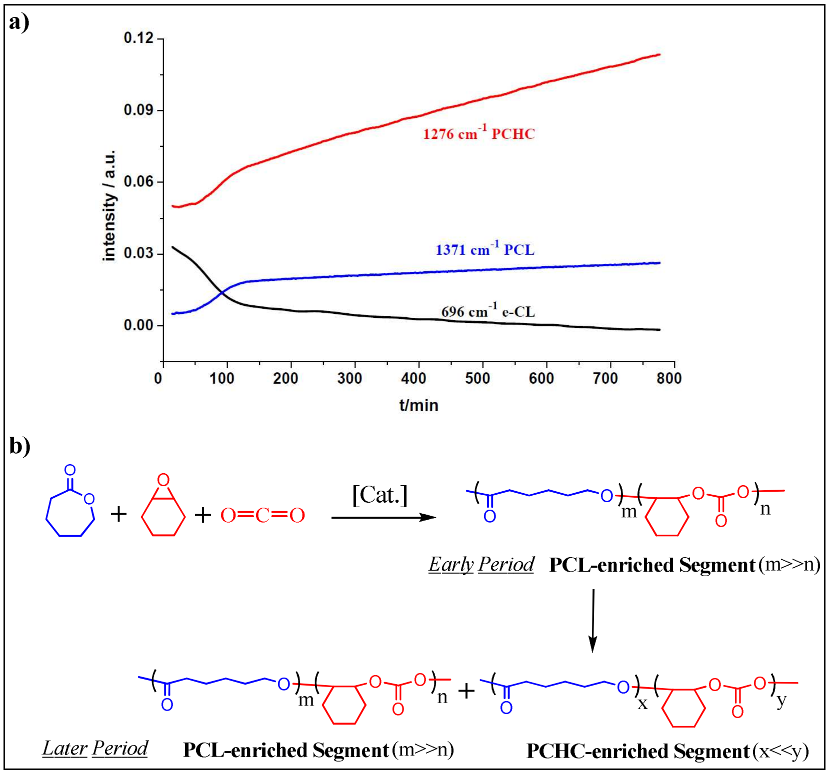

Fig. 7 (a) Time profiles of *in suit* IR absorbance at showing the consumption of ε-CL and the formation of PCL and PCHC. Reaction conditions: 130 mL CHO, 20 mL ε-CL, 0.40 g Cat., 5 MPa, 80 °C. (b) Graphical reaction progress: formation of PCL-enriched segment in early period and PCHC-enriched segment in later period.

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Notes and References

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