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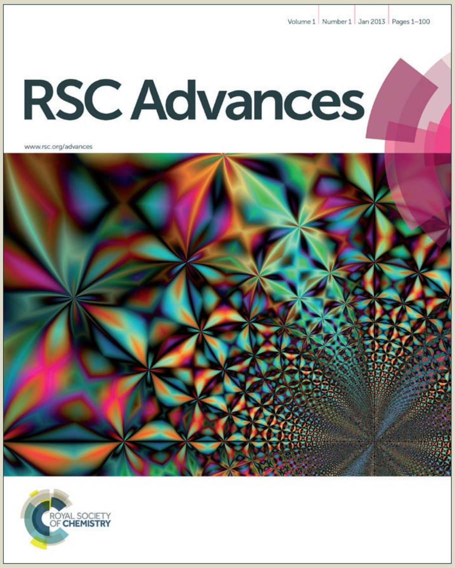

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One-pot Synthesis of High-Molecular-Weight Aliphatic Polycarbonates via Melt Transesterification of Diphenyl Carbonate and Diols using $Zn(OAc)_2$ as Catalyst

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Abstract: A simple and efficient route for one-pot synthesis of high-molecular-weight aliphatic polycarbonates (APCs) by directly melt transesterification of diphenyl carbonate (DPC) with aliphatic diols at equimolar amounts was developed. $Zn(OAc)_2$ was found to be the best catalyst for this reaction among the screened transition metal acetates. The effects of reaction conditions on M_w and yield of the poly(1,4-butylene carbonate) (PBC) were investigated, where the highest M_w of 156200 g/mol with yield of 83 % was obtained under suitable reaction conditions. In addition, based on the results of thermogravimetric and differential thermal analysis (TG-DTA), X-ray diffraction (XRD), scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FT-IR), a plausible reaction mechanism over $Zn(OAc)_2$ was proposed for APCs synthesis.

Keywords: melt transesterification, diphenyl carbonate, aliphatic polycarbonates, $Zn(OAc)_2$, reaction mechanism

1.Introduction

Aliphatic polycarbonates (APCs) as important biodegradable polymers have attracted much attention for their excellent biodegradability, biocompatibility and non-toxicity in recent decades[1,2]. Especially, the high-molecular-weight APCs possess high tensile strength and elongation at break, which are sufficient for the mechanical requirements of biodegradable plastics to solve the problem of white pollution [3-5]. Metal-catalyzed copolymerization of CO_2 with epoxides is a well known approach to obtain such degradable polymers. Among all the catalysts reported, the rare-earth ternary coordination catalysts has been applied in the APCs production in plant since 2004. However, Production and application of APCs on a large scale by this method are still limited by high cost and poor molecular structure [7,8]. Additionally, ring-opening polymerization (ROP) of cyclic carbonates has also received significantly attention for synthesis of APCs . Nevertheless, this route was primarily studied for small-scale biomedical applications due to the high cost of feedstocks [9].

Besides of CO_2/epoxides copolymerisation and ROP discussed above, the transesterification of dialkyl carbonates and aliphatic diols to prepare oligomers in bulk, followed by polycondensation of these oligomers to produce high molecular weight APCs, is a promising route for practical application due to the high efficiency, without any solvent and advantage of synthesizing APCs with diverse structures [10]. Since the pioneering work of Carothes and Natta in 1930 [11], catalysts, including enzyme [12,13], metal oxides [14], inorganic metal salts [15] and organic base [10,16, 17] have been developed. Unfortunately, the molecular weight of these APCs was too low to be used directly as biodegradable plastics. Most recently, Zhu et al. [5]successfully prepared a PBC with maximal M_w value of 176 000g/mol via condensation polymerization of dimethyl carbonate (DMC) and 1,4-butanediol (BD), catalyzed by a TiO_2/SiO_2-based catalyst. Later, Park and coworkers [18] found CH_3ONa was also highly active in this reaction, producing PBC polymer with M_w of 100000-200000 g/mol, and its yield reached 86%.

However, the drawback of the above systems was two-step route necessary, because the first-step transesterification reaction between DMC and aliphatic diols can not carry out at the same conditions with the second step polycondensation reaction for the low boiling point of DMC. Even so, the reaction temperature for first step is also much higher than its boiling point, and excess DMC was required due to evaporation, generally more than 2. Additionally, the most key factor for producing high-molecular-weight APCs in this strategy is that the obtained oligomers in the first step must bear almost equal numbers of hydroxyl and methyl carbonate end groups. Thus, the loss of DMC make it difficult to control the desired molar ratio of end-groups precisely, especially in large scale production industrially. Moreover, the presence of methanol, coproduct, can form an azeotrope with DMC, which is disadvantageous to the separation of the byproduct and the shift of reaction equilibrium. In fact, DPC rather than DMC was usually used to commercially produce aromatic polycarbonates (PC) on a large scale due to its high boiling point [19]. Yamamoto et al.[20] also found that high-molecular-height PBC with M_w of 119000g/mol could also be prepared using equal moles of DPC and BD as feedstocks, though ROP was used in this literature. Obviously, using DPC as feedstock has a distinct advantage over DMC not only in atom-economical but also in the separation and cyclic utilization of co-product.

Transition metal acetates with excellent lewis acid property have been thought to be highly effective catalysts in the reaction of transesterification, carbonylation, glycoysis and so on [21-26]. Simultaneously, divalent transition metal ion with d^{10} electrons could coordinate with many oxygen containing functional groups to reach the stable construction of 18 electrons. Thus, they are also considered to be good initiators or catalysts for copolymer synthesis. Previous literature had already found transition metal acetates were highly active for polyethylene terephthalate (PET) production via melt transesterification of dimethyl terephthalate (DMT) and glycol [27]. Recently, $Cu(OAc)_2$ and $Zn(OAc)_2$ were also found to be able to active cyclic ester monomers and lactide in ROP process to synthesis high-molecular-weight polylactones [28,29]. However, there are few reports involving the application of these compounds as catalysts in APCs synthesis. In this work, we present our results on use of transition metal acetates as catalysts for directly one-pot bulk transesterification of DPC and aliphatic diols at equimolar amounts to one-pot produce high-molecular-weight APCs. Here, the co-product, phenol, can be separated easily and reused in the DPC synthesis via transesterification with DMC or oxidative carbonylation [20].The reaction parameters such as catalyst concentration, reaction temperature and time on the M_w, polydispersity index (PDI) and yield of PBC were investigated in detail to obtain the optimum conditions. Furthermore, a plausible reaction mechanism was proposed based on the results of XRD, TG-DTA, SEM and FT-IR.

2. **Experimental section**

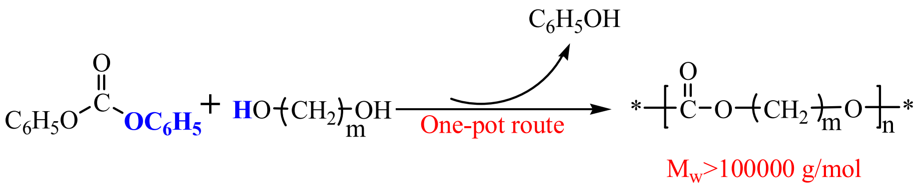
2.1 Materials and reagents

Transition metal acetates obtained from Chengdu Kelong Chemical Reagent Co., Ltd.,(in China) were used without treatment, unless otherwise note. Commercial DPC purchased from Guangdong Guanghua Scitech Co., Ltd., China was purification by recrystallization in absolute ethyl alcohol. All the aliphatic diols including 1,3-propanediol (PPD, 98%), 1,4-butanediol (BD, 98%) , 1,5-pentanediol(PD, 98%) and 1,6-hexanediol (HD, 98%) were dehydrated by distillation over calcium hydride under dry nitrogen gas. Other reagents were of guaranteed grade and used as received.

2.2 General procedure for the synthesis of APCs

The APCs polymer samples were symthesized by one-pot melt transesterification of DPC and diols, as shown in Scheme 1. A typical procedure for synthesis of PBC polymer via this route was performed as follows. The mixtures of DPC (21.41 g, 0.1 mol), BD (9.01 g, 0.1 mol) and stoichiometric ratio of catalyst under a nitrogen atmosphere was placed in a 150 ml three-necked flask, equipped with a mechanical stirrer, reflux condenser and the thermometer. The reaction mixture was heated at reaction temperature under stirring for a certain time untill it became homogeneous. Then a lower pressure (*ca* 200 Pa) was applied slowly over a period of *ca* 20 min to avoid excessive foaming and to carry out the melt transesterification reaction. And the volatile by-products can be removed through the reflux condenser. The PBC polymer was separated by dissolving in CH_2Cl_2 and precipitating with ethanol, and then dried under vacuum

50 °C for 12 h. Others APCs including poly(trimethylene carbonate) (PTMC), poly(pentamethylene carbonate) (PPMC) and poly(hexamethylene carbonate) (PHC) were also synthesized following the similar procedure using corresponding PPD, PD and HD as reactants.



Scheme 1 Preparation of high-molecular-weight APCs via a one pot one-pot melt transesterification of DPC and diols

2.3 Characterization of PBC

The chemical structures of resulted APCs were identified by ^{1}H-NMR. ^{1}H-NMR spectra were acquired in $CDCl_3$ at 25 °C with a Bruker DRX-300 NMR spectrometer.The M_w and PDI of the obtained APCs were determined by gel permeation chromatography (GPC).The GPC measurements were carried out at 30 °C on Waters 515 HPLC system equipped with a 2690D separation module and a 2410 refractive index deter. Tetrahydrofuran (THF) was used as eluent at a flow rate of 0.5ml/min. Polystyrene with a narrow molecular weight distribution were used as standards for calibration.

2.4 **Characterization of catalysts**

XRD analysis was carried out on a PANalytical X’pert pro diffractometer system, using CoKa radiation (0.1789 nm).TGA experiments were carried out using Q600 SDT thermal analysis machine (TA instrument, USA) under a flow of N_2 in the temperature from 50 °C to 550 °C with a heating rate of 10□/min. The morphology of the catalysts was investigated by means of a scanning electron microscope (Inspect F, FEI/Holland). FT-IR spectra were obtained in the range of 400-4000cm^{-1} on a Nicolet-38 FT-IR spectrometer by using KBr pellet technique.

3. Results and discussions

3.1 Catalyst Screening

Table 1 shows the catalytic activities of different transition metal acetates for the melt transesterification of DPC and BD at given conditions. No fraction and polymer was detected during the reaction for free-catalyst system (Entry1 in Table1), implying that catalyst is essential for the melt transesterification process. Among the transition metal acetates, the activity of $Zn(OAc)_2$ is the highest at the given conditions, the M_w of PBC is 93700 g/mol with yield of 85.4 %. One also can see that no obvious difference in M_w and yield for $Zn(OAc)_2.2H_2O$ and $Zn(OAc)_2$, indicating that crystal water has no effect on the PBC synthesis in this process. This is possibly because the temperature of $Zn(OAc)_2.2H_2O$ decompose to $Zn(OAc)_2$ is much lower than that of the reaction proceeded. Compared the result of entry 3 to entry 4, there is also no obvious difference in M_w and yield between the two PBC samples synthesized via two-step route and one-pot process, which would promote researchers to choose a simpler and more convenient alternative. **Fig.S1** shows PBC obtained over $Zn(OAc)_2$ and $Zn(OAc)_2.2H_2O$ special white, but other samples exhibit more or less dark colour. Additionally, some typical catalysts including CH_3ONa [3,18], NaOH[30]and TiO_2/SiO_2(PVP)[5,6] also gave rather poor catalytic performance in this system under identical conditions, though they have been reported to be excellent catalysts in condensation polymerization of DMC and diols in two-step process. $Zn(OAc)_2$ is known to be a green catalyst and has been widely used in fine chemicals synthesis, due to its inexpensive and non-toxic. Therefore, further investigation were carried out using $Zn(OAc)_2$ as catalyst.

Table 1. The catalytic performance of various transition metal acetates for directly melt transesterification of BD and DPC[a]

Entry	Catalysts	M_w ($\times 10^{-3}$ g/mol)	M_w/M_n	Y^d_{PBC} (%)
1	none	-	-	-
2	$Zn(OAc)_2$	93.7	1.71	85.4
3[b]	$Zn(OAc)_2$	9.4	1.53	95.2
4[c]	$Zn(OAc)_2$	92.8	1.69	86.8
5	$Zn(OAc)_2.2H_2O$	91.8	1.67	84.3
6	$Co(OAc)_2$	39.1	1.77	93.5
7	$Cd(OAc)_2$	36.4	1.63	88.6
8	$Mn(OAc)_2$	56.0	1.76	84.2

9	$Cu(OAc)_2$	33.6	1.61	89.3
10	$Pb(OAc)_2$	42.5	1.73	92.5
11	CH_3ONa	50.7	1.56	85.2
12	NaOH	–	–	–
13	TSP-44	41.4	1.45	89.6

[a] Reaction were carried out at 200 °C and 200 Pa for 120 min and the molar ratio of catalyst to DPC was set at 0.2 mol%. [b]reaction time is 15 min (Entry 3). [c] Two-step route was adopted. The mixtures of feedstocks and catalyst in a reactor of 200 °C for 2.0 h under nitrogen atmosphere , while removing phenol at atmosphere pressure, in the first step, then at 200 °C successively under 200 Pa for 2.0 h, in the second step.[d] Yield expressed as a percentage of the theoretical value which was calculated based on the 100% conversion of DPC to PBC.

3.2 Characterization of poly(butylene carbonate)

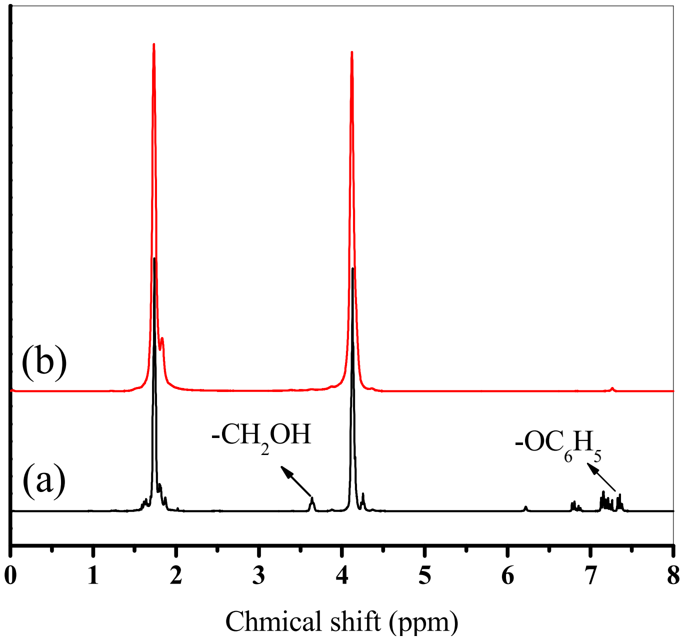


Fig.1 ^{1}H-NMR spectra of (a) PBC (entry 3,Table 1) and of (b) PBC (entry 2,Table 1) polymer obtained via one-pot melt transesterification route

The ^{1}H-NMR spectrum of the obtained PBC samples in $CHCl_3$ is displayed in Fig.1.Two proton signals are observed at 1.74 and 4.12, with equal integration values, which are assigned to middle protons of butylene ($-CH_2CH_2O(CO)O-$) and protons adjacent ($-CH_2O(CO)O-$) to carbonate, respectively. For Fig.1(a), the methylene ($-CH_2OH$) adjacent to end hydroxyl group signals was observed at 3.64 ppm as triplet, and the phenyl （$-C(O)OC_6H_5$）signal was split into three peaks in range of 7.33-7.38 ppm. From the relative intensities of these signals, the proton ratio of [-CH_2OH] to [-$C(O)OC_6H_5$] is approximately 2:5, indicating that oligomers bearing almost equal numbers of phenoxy [-OC_6H_5] and hydroxyl [-OH] end-groups were obtained during the reaction. Thus, we infer that the reaction occurred mostly with the elimination of phenol upon the reaction between the[-$C(O)OC_6H_5$] and [-OH] end groups. As for the ^{1}HNMR spectrum of the generated PBC copolymer (see Fig.1(b)), besides of the two proton signals at 1.74 and 4.12, and no end-group signals was detected. Additionally, no signal at 3.4–3.5 ppm was observed for both ^{1}H-NMR spectra of PBC samples, indicating the absence of any ether linkages (–CH_2–O–CH_2 –) in the polymers, implying without decarboxylation during the melt polycondensation under given conditions [5].The FT-IR spectrum of PBC is presented in **Fig.S2**. The absorption bands appearing 2963 cm^{-1} and 2875 cm^{-1} are attributed to asymmetric and symmetric C-H stretching vibration of methylene, respectively. The strong absorption bands at 1744 cm^{-1} and 1249 cm^{-1}can be ascribed to the stretching and asymmetric stretching vibrations of C=O and O-C-O of the carbonate backbone, respectively [5]. This indicated the ester group of the PBC copolymer.

3.3 Optimization of the reaction conditions

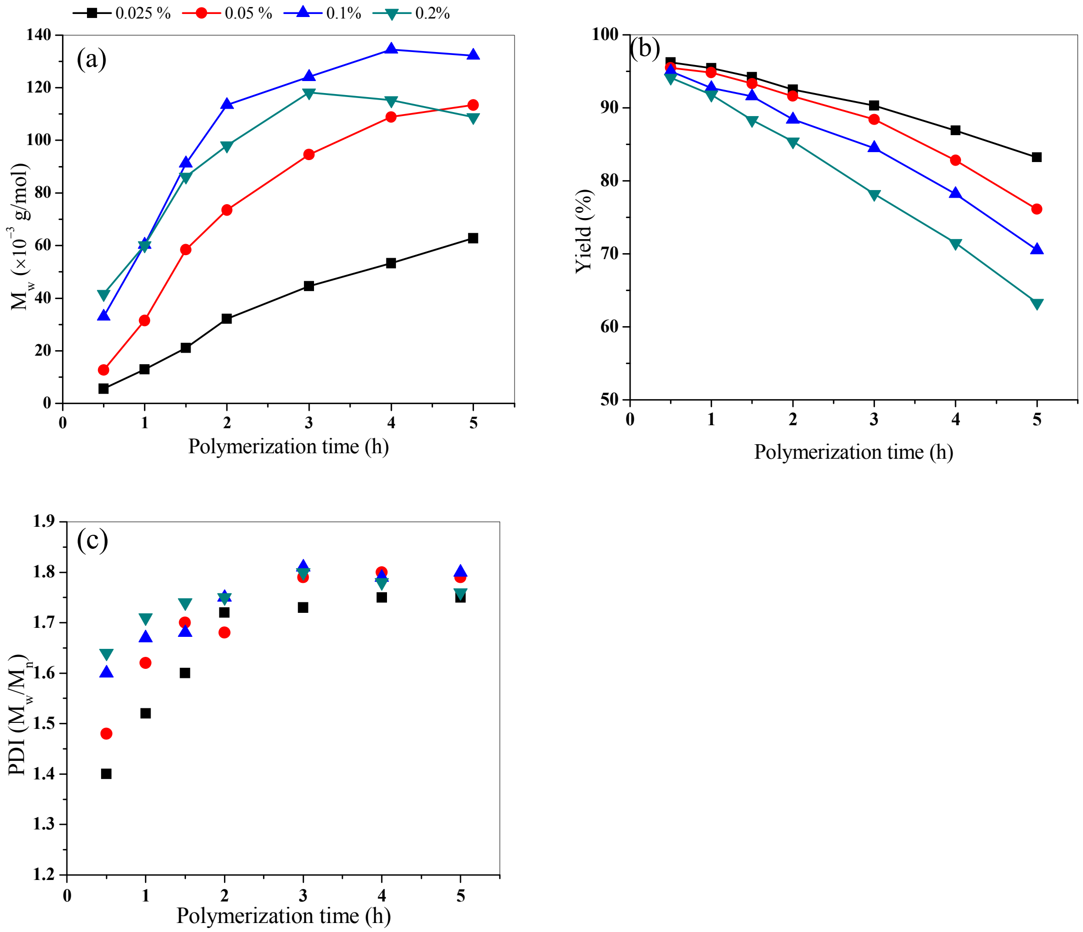


Fig.2 Effect of catalyst concentration on the melt transesterification of DPC and BD. (Reaction conditions: DPC/BD=1:1, temperature 200 °C and pressure of 200 Pa）

In order to optimize reaction conditions, the influence of various reaction parameters was investigated. The impact of the catalyst concentration charged on the PBC synthesis was first examined varying from 0.025 to 0.2 mol% (the molar ratio of Zn(OAc)$_2$ to DPC). As seen in Fig.2 (a), the M_w of PBC increased with increasing catalyst concentration from 0.025 to 0.1mol%, then decreased with further increase the amount of catalyst to 0.2 mol%, which suggested that 0.1mol% catalyst might be sufficient for this process. Additionally, one can see in Fig.2(b) with increasing catalyst concentration and reaction time the yield of PBC decreased, which at least lies in the following two factors. One reason is elimination of phenol during the polymerization reaction. Generally, the higher the $M_{w,}$ the more the phenol removed. The other reason is the decomposition of resulting PBC because the same catalyst also can promote the reverse reaction. There would be completion between the effect of polymerization reaction and that of decomposition or depolymerization reaction. Therefore, as long as the former plays a more dominant role at proper conditions, the molecular weight will increase while its yield decrease all the time. As for the correlation of PDI and catalyst concentration was shown in Fig.2(c), it seems to depend mainly on the M_w of PBC, which gradually increases with increasing M_w. Similar phenomenons on PDI during enzymes-catalyzed synthesis routes were also observed in literature [31].

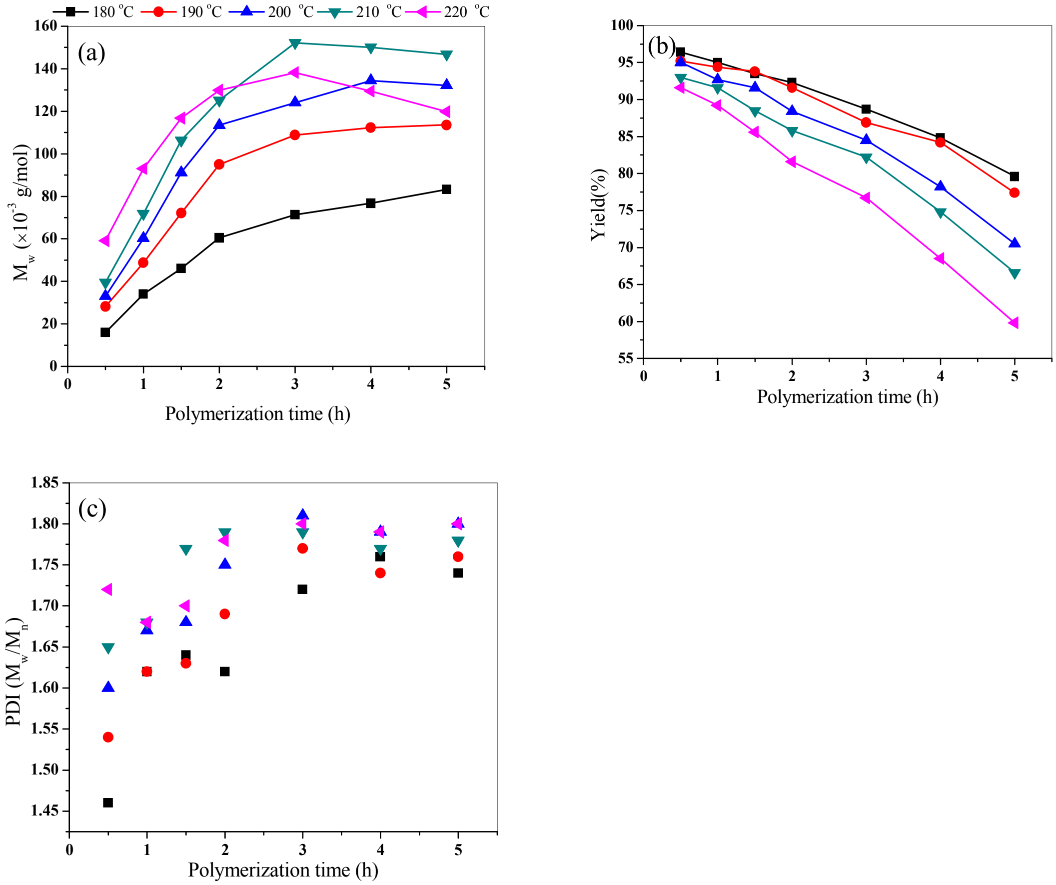


Fig.3 Effect of reaction temperature on the melt transesterification of DPC and BD (Reaction conditions:1:1 DPC/BD；catalyst concentration 0.1 mol% and pressure of 200Pa)

The effect of reaction temperature and time on the catalytic performance were also studied. One can see in Fig.3(a), after reaction at low temperature of 180 °C for 2.0 h, the M_w of PBC was only 60500 g/mol. When the reaction time was prolonged to 5.0, the M_w only increased slightly to 83300 g/mol. However, it significantly increased to 113500 g/mol by raising the temperature to 200°C for 2.0 h, indicating that high reaction temperature can enhance the rate of polycondensation. Further, when the reaction was carried out at 210 °C, the M_w were obviously higher than that at 200 °C, and the maximum M_w of 152600 g/mol was obtained within 3.0 h. Thus, it could be confirmed that the high temperature has a positive effect on promoting this reaction. This can be explained by the fact that higher temperature would reduce the viscosity upon stirring at high shear rates during the synthesis, which might expedite the diffusion-limited polycondensation kinetics [30,32], consequently achieving higher M_w more easily than in lower temperature.Unfortunately, PBC is unstable at higher temperature due to its depolymerization in the presence of catalyst. Meanwhile, too high temperature over a longer time also can led to the consistently decrease of yield and broadening for PDI, as shown in Fig.3(b-c). This may be reasoned that too high temperature could promote the side reaction and thermal degradation of resultant polymer. Therefore, considering M_w and yield comprehensively, 210 °C and 3.0 h were the proper reaction temperature and time for this process.

3.4 Substrate scope

A series of diols substrate were also examined for the synthesis of corresponding APCs in the presence of $Zn(OAc)_2$ with the concentration of 0.1mol % at 210 °C for 3.0 h via this one-step process. The results are summarized in **Table 2**. Except for PPD, the $Zn(OAc)_2$ was found to be application to a variety aliphatic diols, providing the corresponding APCs with high M_w values in high yields. According to literature[33], relatively low activity of PPD can be attributed to the poor thermal stability and side reaction of corresponding PTMC.

Table 2 One-pot synthesis of APCs via melt transesterification of DPC with various diols using $Zn(OAc)_2$ as catalyst[a]

Entry	Substrate	Product	M_w ($\times 10^{-3}$ g/mol)	PDI	Yield (%)
1	PPD	PTMC	39.5	1.43	34.3
2	BD	PBC	152.6	1.72	82.8
3[b]	BD	PBC	142.5	1.71	85.5
4	PD	PPMC	148.8	1.80	89.2
5	HD	PHC	162.4	1.83	92.6
6	BD+HD[c]	PBHC	134.6	1.78	86.3

[a] Reaction were carried out at 210 °C and 200 Pa for 3.0 h and the molar ratio of catalyst to DPC was set at 0.1

mol%.[b] removed catalyst was used at the same weight as entry 2. [c] the molar ratio of BD and HD is 1:1.

To further understand the catalytic performance of $Zn(OAc)_2$ in one-step process, **Table 3** gives a comparison with literature data in terms of M_w value and yield under their optimization reaction for PBC synthesis via different methods. Obviously, the M_w and yield of PBC obtained in the present study are much higher than those of PBC synthesized by ROP of large cyclic carbonates. Moreover, some drawbacks also preclude large-scale preparation of PBC by ROP, such as expensive feedstocks and harmful solvents required, though ROP could be carried out at a relatively low temperature.This result is also superior to that of PBC obtained in TiO_2/SiO_2(PVP) , $Na(Acac)_2$ and BMIM-2-CO_2 catalysis systems. Although the present maximum of 156200 g/mol is evidently inferior to 248000 g/mol that was reported to be the highest date currently, the two-step was necessary in the later reaction. Moreover, this M_w value for the present PBC copolymer is much greater than 70000 g/mol, which are sufficient for the M_w requirements of biodegradable plastics. Therefore, one-pot melt transesterification of DPC and BD with $Zn(OAc)_2$ as catalyst can also considered to be an efficient route for synthesis APCs with high-molecular-weight.

Table 3 Comparison of PBC synthesis in the present study and production of that by other methods

Entry[a]	Original materials（molar ratio）	Catalyst（amount)[b]	Solvent	Temperature[c] / °C	Time[d]/h	M_w[e]/ g/mol	PDI	Yield[f] /%	Ref.
1	BD+triphosgen (3:1)	_	$CHCl_3$	0	12.0	3400	1.70	43	Ref.[34]
2	BD+triphosgen (3:1)	TfOEt (0.5%)	CH_2Cl_2	20	4.0	86400	1.50	29.7	Ref.[34]
3	BD+triphosgen (3:1)	Sec-BuLi(1.0%)	THF	0	1.0	51400	1.46	26.1	Ref.[35]
4	BD+triphosgen (3:1)	HCl+Et_2O (4.0 %)	CH_2Cl_2	25	4.0	11100	1.11	29.4	Ref.[36]
5	BD+DPC (1:1)	Lipase (50.0%)	toluene	120	6.0	119000	2.2	51.5	Ref.[20]
6	BD+DMC (2.0:1)	BMIM-2-CO_2 (1.0%)	_	150	1.0	13900	2.10	_	Ref.[10]
7	DMC/BD (2.5:1)	TSP-44 (0.08 %)	_	200	4.0	81300	1.60	85	Ref.[37]
8	DMC/BD (2.5:1)	TSP-44 (0.08 %)	_	200	4.0	176000	1.80	85	Ref.[5]
9	DMC/BD (1.6:1)	CH_3ONa (0.2%)	_	190	8.0	248000	1.65	86	Ref.[18]
10	DMC/BD(2:1)	Na$(Acac)_2$ (0.02%)	_	_	_	139000	1.76	_	Ref.[4]
11	DPC/BD(1:1)	Zn$(OAc)_2$ (0.10%)	_	210	3.0	156200	1.72	82	This work

[a] Synthetic routes: Phosgene route (Entry 1), ROP (Entry 2-5), two-step process (Entry 6-10). [b] the value of catalyst amounts for entry 5,7 and 8 is mass concentration based on feedstock, entry 10 is also mass concentration based on final polymer, while the rest is molarity. [c] copolymerization temperature. [d] copolymerization time. [e] GPC value. [f] calculated based on BD.

3.5 Results of catalysts characterization

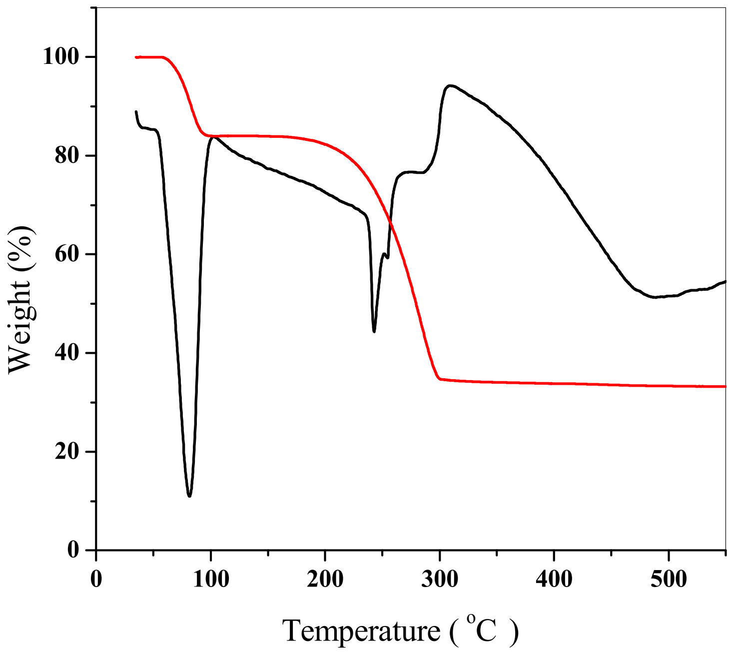


Fig.4 TG-DTA curves of $Zn(OAc)_2.2H_2O$

From TG-DTA profiles shown in **Fig. 4**, one can clearly see the temperature at which phase transformation took place. A dramatic weight loss (ca.16 wt%) due to dehydration of the $Zn(OAc)_2.2H_2O$ occurred from 50 to 100 °C, accompanied with a strong endothermic peak centred at 95□. The second stage ranges from 220 to 330 °C and the weight loss is about 73 % with a endothermic peak at 249 °C, which was caused to the decomposition of $Zn(OAc)_2$ to ZnO. The result is good in accord with previous papers[21]. From 320 to 450 °C, some obvious exothermic or endothermic peak appeared, whereas no weight loss phenomenon can be observed. It is reported that $Zn(OAc)_2$ was initially converted to acetic anhydride and ZnO, and then the acetic anhydride could be decomposed into CO_2 and H_2O [38]. Therefore, the exothermic peak in higher temperature can be ascribed to the degradation of acetic anhydride. These results indicate that $Zn(OAc)_2$.$2H_2O$ will decompose into $Zn(OAc)_2$ during the reaction and $Zn(OAc)_2$ remains its structure even after reaction at 210 °C.

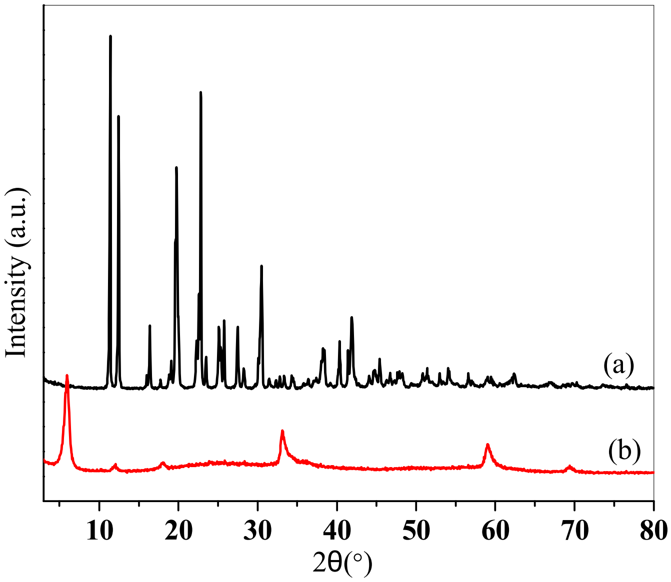


Fig.5 XRD patterns of (a) fresh and (b)used catalyst

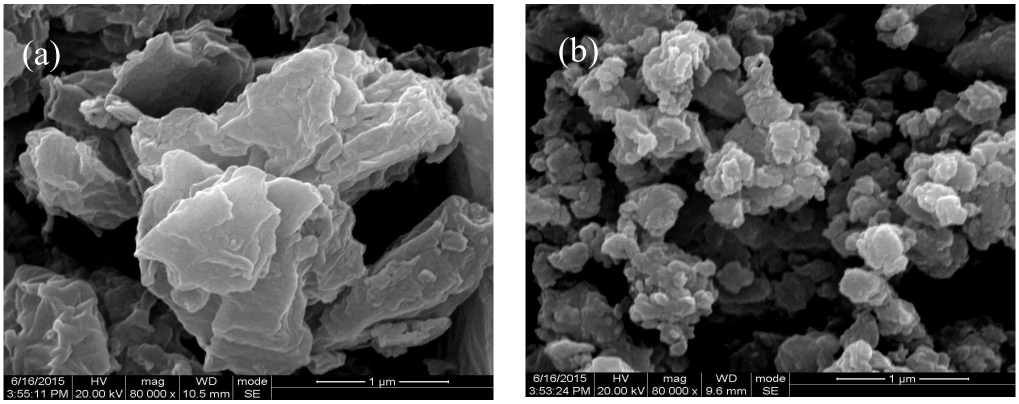


Fig.6 SEM photographs of (a) fresh and (b)used catalyst

The used catalyst was obtained by filtering the CH_2Cl_2 solution of the resulting copolymer, then washed sequentially with CH_2Cl_2 for several times, and dried in vacuo at room temperature for 24 h. **Fig.5** displays the XRD of the fresh and used catalyst. Obviously, a large structural change appeared between the two samples.The fresh catalyst was the typical crystal structure of $Zn(OAc)_2$. (PDF:33-1464) before the reaction, but the used catalyst can be proved to be $Zn_5(OH)_8(OAc)_2.2H_2O$by XRD[38]. In such a new zinc species, the carboxylate group coordinate to Zn^{2+} as a unidentate ligand [39], which also had excellent catalytic performance to this reaction (**see entry 3 in Table 2**). In their SEM micrographs (**Fig.6),** great difference can be observed between these two samples. It can be seen that the commercial $Zn(OAc)_2$ presents a more exfoliated morphology, while the used catalyst particles is built in aggregates, the particle size of the later is evidently much smaller than that of former, which may be resulted from the recrystallization and even recombination of Zn^{2+} and CH_3CCOO^-. Thus, $Zn(OAc)_2$ appeared to be dissolved in the reactants as a homogeneous catalyst or precursor for this reaction.

3.6 Possible reaction mechanism

The interactions of reactants with catalyst were further examined using IR spectra to investigate the plausible reaction mechanism, the results are illustrated in Fig.7. The FTIR of $Zn(OAc)_2$ (Fig.7a) has spectral bands at 1456 and 1560 cm^{-1} that are assigned to carboxyl strething frequencies of asymmetry ($\nu_a(COO^-)$) and symmetry ($\nu_s(COO^-)$) for the bidentate carboxylate group to Zn^{2+} [21-24], as displayed in Scheme 1 (Species A). The sample for IR analysis was prepared by mixing of BD and $Zn(OAc)_2$ at molar ratio of 2:1 then pretreatment under the conditions of the reduced pressure of 200 Pa and 200°C for 2.0 h. As displayed in Fig.7c, new strong bands at 1737 cm^{-1} and 1260 cm^{-1} were observed, which could be assigned to the appearance of C=O and C-O stretching modes of monodentate carboxylate groups [21,22]. Simultaneously, the $\nu_a(COO^-)$ band for shifts to 1598 cm^{-1} and that of $\nu_s(COO^-)$ band was found to have a red shift to 1439 cm^{-1}. This difference of $\nu_s(COO^-)$ and $\nu_a(COO^-)$ was 160 cm^{-1}, while the value for $Zn(OAc)_2$ was only 104 cm^{-1}. This demonstrated that the coordination mode of the Zn^{2+} and acetate groups changes from bidentate coordination to monodentate coordination, leading to the formation of a new Zn-complex[40].

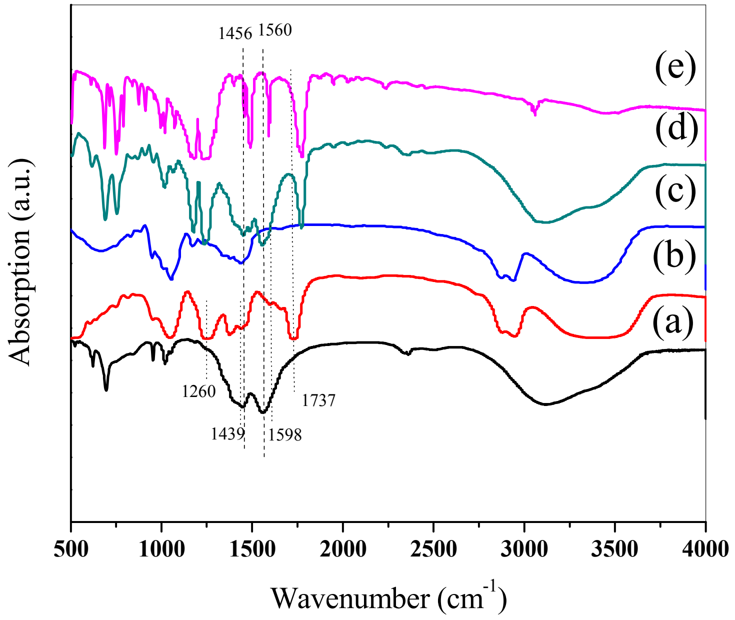
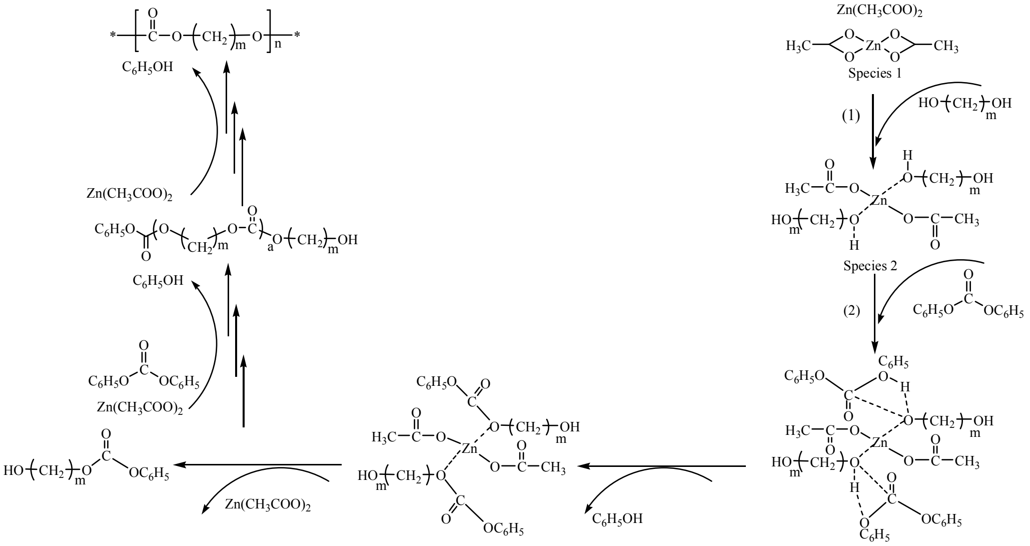


Fig.7 FT-IR spectra of (a) $Zn(OAc)_2$; (b) mixtures of $Zn(OAc)_2$ and BD at molar ratio of 1:2 treatment at 200 °C for 2.0 h in reduced pressure ; (c) BD; (d) mixtures of $Zn(OAc)_2$ and DPC at molar ratio of 1:2 treatment at 200 °C for 2.0 h in reduced pressure and (e) DPC

DPC did not seem to interact with $Zn(OAc)_2$ directly, no new characteristic bands, which were related to the activation of the carbonyl in DPC, were observed , though the mixtures of DPC and $Zn(OAc)_2$ were also pretreated according to the same process as the sample of BD and $Zn(OAc)_2$.This conclusion was also further confirmed by the fact that no change could be observed in Fig.7(d) compared with the spectrum of DPC and $Zn(OAc)_2$. Using $Zn(OAc)_2$ as a catalyst for the reaction of 1,5-naphthalenediamine (NDA) and DMC, Xiao et al. have proposed that what activated the carbonyl of DMC was an intermediate zinc complex rather than $Zn(OAc)_2$[40].The new zinc coordinated complex was the resultant of the interaction between nitrogen atoms of amino in NDA and Zn^{2+} of $Zn(OAc)_2$. Coordination chemistry revealed that the oxygen atoms of carbonyl and phenoxy in DPC as well as that of hydroxyl in diols molecule all had a chance to coordinate with Zn^{2+}, which was usually explained by the fact that the lone electron pair of an oxygen atom can also occupy the empty d-orbital of the zinc atom in the acetate molecule to form a new zinc complex [41,42]. The optimized structures and charge analysis of reactants by Hyperchem 7.5 based on AM1 semiempirical method are displayed in

Fig.S3 and their electron densities were -0.335,-0.560, -0.531, and -0.689 of negative charge, respectively. This meant that the oxygen atom of hydroxyl in1,4-butanediol molecule was more possible than that of DPC molecular to coordinate with Zn^{2+} ion. This theoretical arithmetic results is in a good accord with the experimental result in **Fig.7**. Moreover, the similar result has also been found in many literature that the presence of hydroxyl could help transform the bidentate coordinate of $Zn(OAc)_2$ into monodentate coordination and then facilitated the activation of carbonyl[21,40]. Therefore, based on the published reports and the results in this work, a probable reaction mechanism for one-pot melt transesterification of DPC and aliphatic diols was proposed and depicted in **Scheme 2**.



Scheme 2 Proposed mechanism for one-pot synthesis of APCs via melt transesterification route

Conclusions

In summary, melt transesterification of DPC and various diols with equal mole quantities using $Zn(OAc)_2$ as catalyst is a facile and general synthesis strategy for one-pot production of APCs with M_w greater than 100000 g/mol. The optimal condition was set as follows: the catalyst concentration of 0.1mol%, temperature of 210 °C and reaction time of 3.0 h. Compared with using DMC as feedstock in two-step process, using DPC as a raw material is operatively simple and has much higher atomic economy. XRD and FT-IR revealed that BD was activated by Zn^{2+} via the coordination of oxygen atom in hydroxyl group.

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