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Terpolymerization of Carbon Dioxide with Propylene Oxide and ε-Caprolactone: Synthesis, Characterization and Biodegradability

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Summary

An aliphatic polycarbonate, terpolymer of carbon dioxide, propylene oxide and ε-caprolactone(PPC-CL-PPO-CL),was synthesized by using a polymer supported bimetallic complex as a catalyst. The terpolymers prepared were characterized by FTIR, ^{1}H NMR, ^{13}C NMR, DSC and WAXD measurements. The influences of various reaction conditions such as molar ratio of the monomers, reaction time and reaction temperature on the terpolymerization progress were investigated. The results showed that ε-caprolactone (ε-CL) was inserted into the backbone of poly(propylene carbonate)-poly(propylene oxide) (PPC-PPO) successfully. The viscosity and glass transition temperature of the terpolymers were much higher than PPC-PPO. ε-Caprolactone offered an ester structural unit that gave the terpolymers remarkable degradability. And the degradation rate of the backbone increased with the ε-CL inserted into the terpolymers.

Keywords:

carbon dioxide, propylene oxide, ε-caprolactone, terpolymerization, degradable

Introduction

Carbon dioxide (CO_2) is considered the major greenhouse gas responsible for global warming, which may contribute to the climate change [1-4]. Thus CO_2 capture and utilization are actively investigated in many options. One possible utilization approach is to convert CO_2 resources to polymeric materials and use them in industry fields. Since the pioneering work of Inoue in 1969[5], the synthesis of aliphatic polycarbonates from carbon dioxide and epoxides has been a long-standing interest as a potential way to carbon dioxide utilization [6-9].

In order to improve the thermal properties and degradability of aliphatic polycarbonates, various monomers were introduced into the copolymerization of carbon dioxide and propylene oxide (PO). In our previous work we synthesized poly[(propylene oxide)-co-(carbon dioxide)–co-(γ-butyrolactone)],which showed remarkable degradability than PPC-PPO[10]. The drug control and release abilities have also been investigated [11]. Yang SY [12] found that ε-caprolactone offered certain aliphatic structural units making the copolymers biodegradable. Hwang Y [13] synthesized poly(propylene carbonate-co-caprolactone) which contained blocked ε-CL units as well as PC linked ε-CL units by using zinc glutarate catalyst. However the products were crystalline and showed low glass transition temperatures. In the present work, we used the polymer-supported bimetallic catalyst to ensue the terpolymerization of ε-caprolactone with carbon dioxide and propylene oxide .The ring-opened ε-CL units were found to be linked to the propylene carbonates directly and no blocked CL was detectived, giving the polymers amorphous structures. The novel aliphatic carbonates showed high glass transition temperatures and good degradability.

Experimental

Materials

ε-Caprolactone (ε-CL) was purchased from Daicel and distilled before use. PO (Shanghai Chemical Reagents Co., A.R. grade) and toluene (Hengyang Organic Chemical Reagents Plant, A.R. grade) were dehydrated by 0.4 nm molecular sieves prior to use. Carbon dioxide (purity more than 99.5%) was used as received. All other reagents and solvents were analytical grade and used without further purification.

Instruments

FTIR spectra was recorded on Nicolet AVATAR360 FT-IR spectrometer. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Varian Inova-400 spectrometer with $CDCl_3$ as solvent, the molar fractions of CO_2, PO and CL were calculated by integrating areas. The glass transition temperature (T_g) of the copolymers were determined by different scanning calorimetry (DSC) on a TA DSC-Q10 instrument. The temperature range was from -20°C to 100°C and the heating rate was 10°C/min in nitrogen atmosphere. Intrinsic viscosity [η] measurements were carried out in benzene at 35±0.1°C using an Ubbelohde suspended level capillary viscometer. The molecular weight was calculated from the equation($[\eta]=1.11\times10^{-4}[M_n]^{0.8}$(dL/g))[14].Elemental analysis were carried out on a Elementar Vario ELⅢ instrument.

Preparation of catalyst

The polymer-supported bimetallic complex (PBM) was used as a catalyst for the terpolymerization of CO_2, PO and CL, and was synthesized according to the literature 6, 8, 15. For example, $ZnCl_2$ (2.436 g) and poly(ethylene glycol) (M_w 600) (36.974 g) were mixed in a 500ml beaker. $K_3Fe(CN)_6$ (1.646 g) was dissolved in distilled water. Both solutions were mixed under vigorous stirring and the precipitate was filtered, collected, washed with distilled water, and dried under vacuum till constant weight. The resulting fine yellow powder was then stored until use.

Preparation of aliphatic polycarbonates

Terpolymerization of CO_2, PO and ε-CL was performed in a 300 ml stainless steel autoclave equipped with a magnetic stirrer. The reactor was connected to dry nitrogen and CO_2 cylinder using a three-way valve. Required amount of the catalyst, PO, ε-CL and toluene were added into the autoclave after the connection pipelines were cleaned out with dry nitrogen gas. The autoclave was then pressurized to 4 MPa by a CO_2 cylinder. The reaction mixture was stirred magnetically at desired temperature for a certain period. When the reaction was finished, the reactor was cooled to room temperature, and the pressure was released. The resulting viscous mixture was collected after toluene and excess PO were evacuated. The mixture was then washed with C_2H_5OH, which contained 5% HCl, and three times with only C_2H_5OH.The precipitate was dried under vacuum till constant weight. For purification, the resulting polymer was dissolved in a proper volume of methylene chloride. The residual catalyst was removed from the product solution by filtering. Finally, the polymer was precipitated by pouring the concentrated solution into vigorously stirred methanol. The methanol-insoluble product was centrifuged and dried for 2 days at room temperature under vacuum.

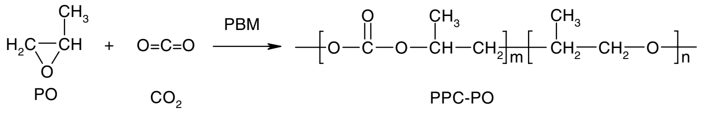
The copolymer of carbon dioxide and propylene oxide(PPC-PPO) was synthesized in the same procedure, except that no CL was added into the polymerization.

Degradation experiments

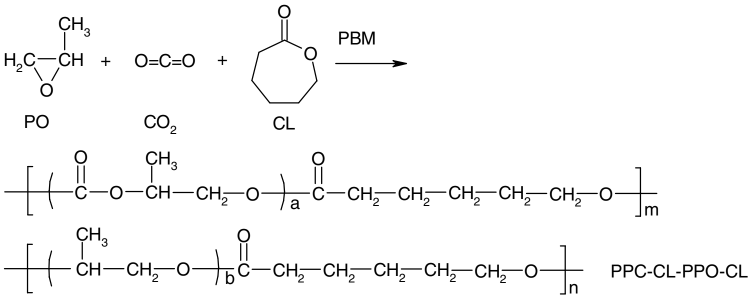
Hydrolysis tests were performed to appraise the copolymers' degradability. The copolymers were dissolved in CH_2Cl_2 to make 8 wt% solutions and formed thin films about 1mm thick on polytetrafluoroethylene templates after the volatilization of the solvent. The thin films were dried under vacuum at 35°C till constant weight. Then they were put in vials filled with PH7.4 phosphate-buffered saline solution (PBS) and placed in a thermostat for various periods at 37°C.The degradability of the copolymers were determined through total weight loss of the films over a certain time.

Results and discussion

Structural Characterization of Polymers



Scheme 1. Copolymerization of Carbon Dioxide with Propylene oxide



Scheme 2. Terpolymerization of Carbon Dioxide with Propylene oxide and ε-Caprolactone

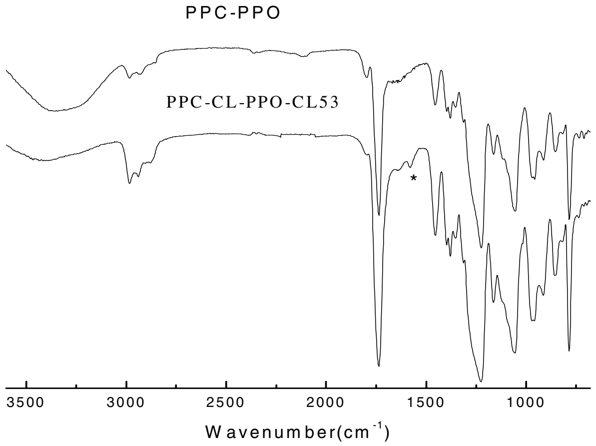


Figure 1. FTIR spectra of PPC-PPO and PPC-CL-PPO-CL53

PPC-PPO and PPC-CL-PPO-CL53 were used as samples for the FTIR, ^{1}HNMR and ^{13}CNMR characterization.

The FT-IR spectra of PPC-PPO and PPC-CL-PPO-CL53 are shown in Figure 1. Strong absorptions at 1736 and 1225 cm^{-1} were ascribed to C=O and C-O stretching vibration of the oxycarbonyloxy group, respectively, indicated that incorporation of CO_2 into polymer chain. The asterisk-marked peak in FT-IR spectra of PPC-CL-PPO-CL at 1570 cm^{-1} was found to be responsible for the asymmetric stretching vibration of $-CO_2^-$ carbonxylate ions [16], indicating the presence of carboxylate ions in PPC-CL-PPO-CL.

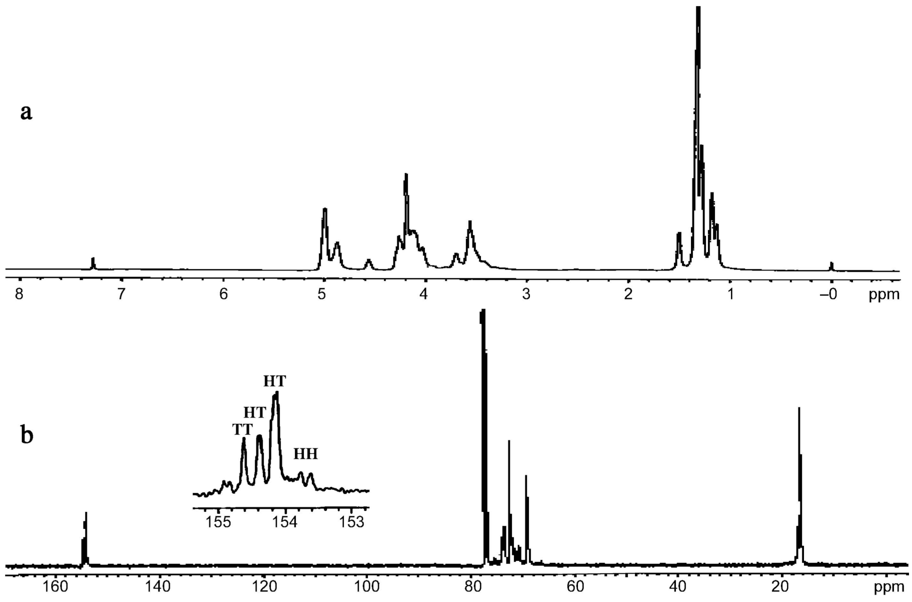


Figure 2. ^{1}HNMR and ^{13}CNMR spectra of PPC-PPO

The ^{1}HNMR spectra of PPC-PPO is shown in figure 2a. The ^{1}HNMR spectra confirmed the existence of carbonate link: ^{1}HNMR(δ,$CDCl_3$), 1.2(d, CH_3), 5.0(m, $CH(CO_3)$), 4.2(m, $CH_2(CO_3)$).The signals at 3.5 ppm and 1.34 ppm were assigned to the hydrogens in ether linkage of propylene oxide. The characteristic proton chemical shifts of carbonate link and ether link of propylene oxide were also observed in the ^{1}HNMR spectra of PPC-CL-PPO-CL(Figure3a):δ1.2[3H,CH_3(a)], 5.0[1H,CH (CO_3),(b)],4.2[2H,$CH_2(CO_3)$(c)],1.34[3H,CH_3(a')],3.4-3.6 [3H,CH_2CH,(b',c')].

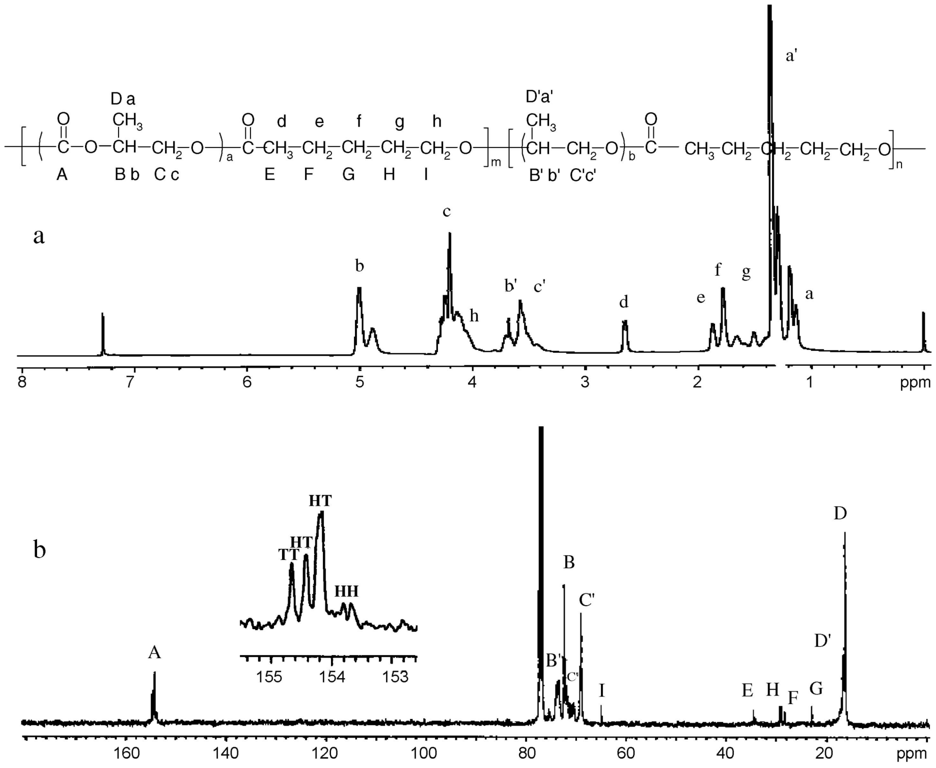


Figure 3. ^{1}HNMR and ^{13}CNMR spectra of a PPC-CL-PPO-CL terpolymer prepared by CO_2 terpolymerization with PO and ε-CL in 5:3 feed molar ratio

According to literatures reported previous [13], the peaks at 2.3,1.6-1.7,1.8,4.0 ppm in the ^{1}H NMR spectra originated from blocked CL units, while the peaks at 2.6,1.6-1.7,1.8 and 4.1 ppm originated from CL units directly linked to PC(polycarbonate) units. The signals that appeared in the ^{1}H NMR spectra of PPC- CL-PPO-CL accorded with the characteristic peaks of PC-linked CL units reported by Hwang Y[13]. The signals of ring-opened CL linked to PC were listed as follows: δ2.6[2H,CH_2(d)], 1.8 [2H,CH_2(e)], 1.6-1.7 [4H,CH_2(f), CH_2(g)], 4.1[2H,CH_2(h)]. It was also possible that the CL units inserted into PPO parts. And the chemical shifts of PPO-linked CL units might be close to that of PC-linked CL units. The proposed structure was showed in Figure 3a. There's no signal at 2.3ppm, revealing that no PCL was synthesized as byproduct. In a word, all the information showed that there was no blocked CL units or PCL in the product. Proton peak (δ4.58) in the ^{1}HNMR spectra of PPC-PPO indicated that cyclic carbonates formed as co-products. However, the signals were not observed in the ^{1}HNMR spectra of PPC-CL-PPO-CL (Figure 3a). It seemed that the introduction of CL could restrain the synthesis of cyclic carbonates.

The ^{13}CNMR spectra of PPC-PPO and PPC-CL-PPO-CL53 are shown in Figure2b and Figure3b respectively. The main signals for PPC-PPO were assigned as follows:153-155(CO_3),72.3(CH),70.5(CH),16.2(CH_3). The signals for PPC-CL-PPO-CL53 were assigned as follows:δ153-155[OCOO(A)] , 72.3[CH(B)] , 70.4 [CH_2(C)], 16.2[CH_3(D)]. Signals of ring-opened ε-CL: 34.5[CH_2,(E)], 28.3[CH_2, (F)], 22.9[CH_2,(G)], 29.3[CH_2, (H)], 64.3 [CH_2, (I)].Ether linkage of propylene oxide: δ73.7[CH(B')], 72.1[CH_2(C')], 16.5[CH_3(D')].

The carbonate carbon signals of PPC-PPO and PPC-CL-PPO-CL53 were both magnified and shown in the figures. There were peaks at 153.7, 154.2, 154.4, 154.7. According to the literatures reported previous[17]. Three regions were assigned as HT(154.2and154.4), TT(154.7), HH(153.7) for alternative chain segments. The figures revealed that HT junctions were predominant junctions in both PPC-PPO and PPC-CL-PPO-CL.

The FTIR, ^{1}HNMR and ^{13}CNMR spectras confirmed that ε-CL was ring opened and inserted into the backbone of PPC-PPO successfully.

According to the integration of the ^{1}HNMR spectras of the copolymers, the molar fractions of CO_2(f_{CO_2}) in PPC-PPO was 41.2%,while f_{CO_2} in PPC-CL-PPO-CL terpolylmers were lower than that. The decrease of f_{CL} was due to the introduction of the third monomer in the backbone. As the amount of ε-CL fed in the reactions increased, the molar fractions of CO_2 and ε-CL(f_{CL}) increased. f_{CL} had a maximum value of 9.78% when PO:CL ratio reached 5:3. However, as the CL amount fed in the reaction went on increasing, f_{CL} decreased. It was considered that the transformation efficiency was high when the amount of CL fed in the reactions was not very large. But as the CL content went on increasing, the amount of dissociative ε-CL increased.

Table 1. Influence of PO:CL molar ratio on composition of the polymers

Polymer	PO:CL (molar ratio)	Composition[a](molar fraction in %)			Elemental Analysis(%)			
		f_{CO_2}	f_{CL}	f_{PO}		C	H	O
PPC-PPO	5:0	41.2	0.00	58.8	Calcd	48.28	6.04	45.68
					Found	47.73	6.08	46.19
PPC-CL-PPO-CL51	5:1	37.2	5.46	57.3	Calcd	49.15	6.41	44.44
					Found	49.18	6.23	44.59
PPC-CL-PPO-CL52	5:2	37.5	7.49	55.0	Calcd	49.10	6.34	44.56
					Found	49.05	6.04	44.91
PPC-CL-PPO-CL53	5:3	37.4	9.78	52.8	Calcd	49.15	6.31	44.54
					Found	49.17	6.41	44.42
PPC-CL-PPO-CL54	5:4	37.7	7.57	54.7	Calcd	49.01	6.32	44.67
					Found	50.07	6.34	43.59
PPC-CL-PPO-CL55	5:5	38.6	6.25	55.2	Calcd	48.74	6.32	44.94
					Found	48.78	6.16	45.06

Reaction conditions :T=60°C; t=24h

[a]The molar fractions of CO_2, PO and ε-CL calculated by integrating areas of ^{1}HNMR spectras of PPC-PPO and PPC-CL-PPO-CL

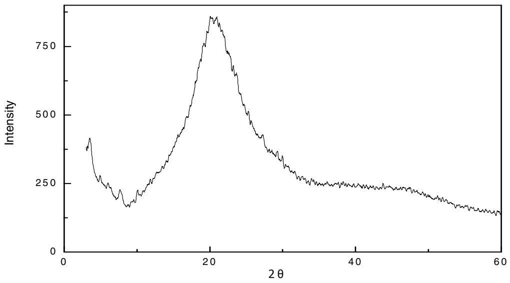


Figure 4. The wide-angle X-ray diffraction spectra of PPC-CL-PPO-CL

Because CL was easier to coordinate with the catalyst than PO. Moreover, excess ε-CL would surround the active centers and prevent PO from contacting with the active centers. In addition, ε-CL and CO_2 could not copolymerize under the reaction conditions. Thus, excess ε-CL hampered the reactions and resulted in the decrease of f_{CL}.
The elemental analysis data for PPC-PPO and PPC-CL-PPO-CL are listed in Table 1. The results revealed that the calculated data of elemental contents were close to the found data. The differences were not significant.
The PPC-CL-PPO-CL terpolymers revealed only a single T_g and no crystalline melting point(Figure5 and Fiurer6), indicating that the terpolymers were amorphous. The wide-angle X-ray diffraction spectra(Figure 4) also confirmed the conclusion and demonstrated that there was no ε-CL homopolymer or blocked ε-CL in the products.

Influence of PO:CL molar ratio

Table 2 shows the influence of PO:CL molar ratio on the properties of the terpolylmers. The [η], M_v and T_g are all related to the structure and components of the terpolymers. The T_g of the PPC-CL-PPO-CL terpolymers were higher than that of PPC-PPO. The [η] and M_v also increased with the increase in the amount of CL contented in the terpolymers(the CL molar fractions were listed in Table 1) .It was considered that the introduction of CL had positive effect on raising T_g and [η].

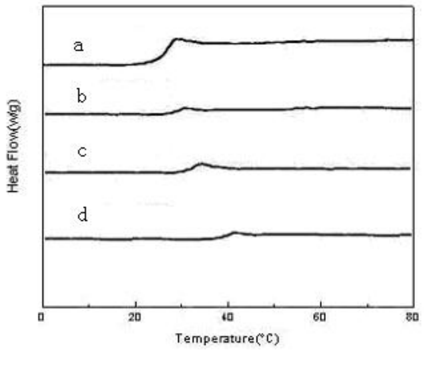


Figure 5. DSC curves of polymers prepared from different PO:CL molar ratio(a.PPC-PPO;b.PPC-CL-PPO-CL51;c.PPC-CL-PPO-CL52;d.PPC-CL-PPO-CL53)

Table 2. Influence of PO:CL molar ratio on terpolymerization

Polymer	PO:CL (mol:mol)	Yield (g/g of cata.)[a]	[η] dL/g	M_v(×10^4)	T_g(°C)
PPC-PPO	5:0	46.5	0.442	3.16	27.5
PPC-CL-PPO-CL51	5:1	40.2	0.556	4.21	30.6
PPC-CL-PPO-CL52	5:2	38.6	0.618	4.81	34.8
PPC-CL-PPO-CL53	5:3	36.3	0.724	5.86	41.2

Reaction conditions :T=60°C; t=24h;1.0g catalyst.
[a] Yield of polymer insoluble in methanol.

Influences of reaction time and reaction temperature

The influence of reaction time on T_g, [η] and M_v is shown in Table 3.The longer the reaction time was, the higher the [η] Mv and T_g of the terpolymers were. However, when the reaction time was prolonged to 60 hours, both [η] and T_g declined. It was found that the relation between the molecular weight and reaction time accorded with the mechanism of anionic coordination polymerization[18].It was explained as that the terpolymerization had a certain induction period. The velocity of the reaction was speeded after the induction period. At the same time the heat was released and the molecular weight reached a maximum value. However, as the reaction time was over-prolonged, the velocities of chain transfer and decomposition would beyond the normal value, and resulted in the decline of [η] and M_v.

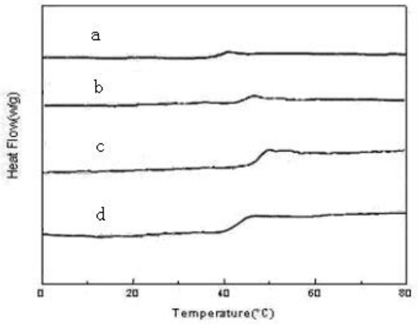


Figure 6. DSC curves of terpolymers prepared from different reaction time(a.12h; b.24h; c.36h; d.48h)

Table 3. Influence of reaction time on terpolymerization

Polymer	Reaction Time(h)	Yield (g/g of cata.)[a]	[η] (dL/g)	M_v (×10^4)	T_g(°C)
PPC-CL-PPO-CL24	24	36.3	0.724	5.86	41.2
PPC-CL-PPO-CL36	36	38.9	0.815	6.80	45.8
PPC-CL-PPO-CL48	48	39.4	0.869	7.36	48.6
PPC-CL-PPO-CL60	60	34.5	0.752	6.15	43.1

Reaction conditions :T=60°C; PO:CL ratio=5:3;1.0g catalyst.
[a] Yield of polymer insoluble in methanol.

Table 4. Influence of reaction temperature on terpolymerization

Polymer	Reaction Temperature (°C)	Yield (g/g of cata.)[a]	[η] dL/g	$M_v(\times10^4)$
PPC-CL-PPO-CLa	50	15.1	0.195	1.14
PPC-CL-PPO-CLb	60	36.3	0.724	5.86
PPC-CL-PPO-CLc	70	39.6	0.826	6.91
PPC-CL-PPO-CLd	80	17.2	0.205	1.21
PPC-CL-PPO-CLe	90	12.6	0.187	1.08

Reaction conditions : t=24h; PO:CL ratio=5:3; 1.0g catalyst.

[a] Yield of polymer insoluble in methanol.

The influence of reaction temperature on the terpolymerization was investigated with temperature change from 50°C to 90°C.The results are summarized in Table 4. At 50°C the [η] of the resulting polymer was only 0.195 dL/g. The intrinsic viscosity increased as the reaction temperature changed from 50°C to 70°C and it had maximum value at 70°C.Then the intrinsic viscosity dropped rapidly when the temperature was increased from 70°C to 90°C.That is because higher temperature was benefit to reduce the induction period and accelerate the reaction speed. However when the temperature was higher than 70°C, the catalyst was easy to decompose, resulting in the decline of intrinsic viscosity and molecule weight. The optimal terpolymerization temperature was between 60°C and 70°C.

Degradability of the polymers

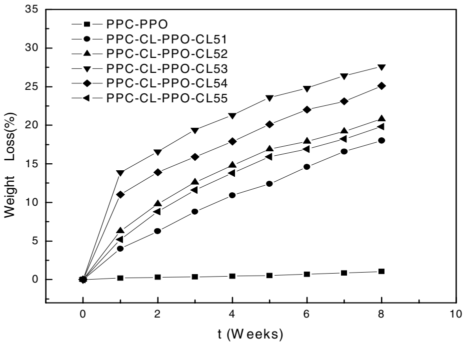


Figure 7. Influence of PO:CL ratio on the degradabilities of PPC-CL-PPO-CL terpolymers

The degradability of the terpolymers synthesized from various PO:CL ratios were determined in order to evaluate the influence of ε-CL content. Figure 7 revealed that the hydrolytic activities of PPC-CL-PPO-CL terpolymers were much stronger than PPC-PPO. This could be due to the introduction of the hydrolytic ester units that in ε-CL. It can be seen that PPC-CL-PPO-CL53 had the best degradability which contained the most molar fraction of CL(9.78%).The higher the molar fraction of ε-CL ,the higher the hydrolytic activity was. However, the mechanism of the degradation is still not very clear. It will be further studied in our future work.

Conclusion

PPC-CL-PPO-CL terpolymerized from CO_2, PO and ε-CL was successfully synthesized using polymer supported bimetallic complex as a catalyst . The introduction of ε-CL in the terpolymers positively improved [η] and M_v, tuning the T_g of the terpolylmers. The T_g of PPC-CL-PPO-CL was high as high as 48.6°C while the T_g of PPC-PPO was only 27.5°C.The PPC-CL-PPO-CL terpolylmers showed remarkable degradability. The weight loss of PPC-CL-PPO-CL53 was 27.6% after 8 weeks in buffer solution immersion test. In contrast, PPC-PPO itself exhibited a very tiny weight loss .The PPC-CL-PPO-CL terpolymers showed potential applications in drug release and other fields requiring hydrolysable materials.

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