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Double propagation based on diepoxide, a facile route to high molecular weight poly(propylene carbonate)

Youhua Tao [a,b], Xianhong Wang [a,b,*], Xiaojiang Zhao [a,b], Ji Li [a,b], Fosong Wang [a,b]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renming Street 5625, Changchun, Jilin 130022, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

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Abstract

Poly(propylene carbonate) (PPC) with number average molecular weight (M_n) higher than 200 kg/mol was prepared via the terpolymerization of carbon dioxide, propylene oxide and diepoxide using $Y(CCl_3OO)_3-ZnEt_2$−glycerine coordination catalyst. When equimolar $ZnEt_2$ and diepoxide were used, double propagation active species were generated in situ by nucleophilic attack of metal alkoxide on diepoxide, leading to PPC of doubled M_n value. The molecular weight of PPC has dramatic influence on its thermal and mechanical performances. PPC with M_n of 227 kg/mol showed modulus of 6900 MPa, while the modulus of PPC with M_n of 109 kg/mol was only 4300 MPa. Moreover, when M_n increased from 109 to 227 kg/mol, a 37 °C increase of the onset degradation temperature was observed.

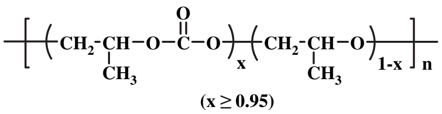
Keywords: Carbon dioxide; Diepoxide; Poly(propylene carbonate)

1. Introduction

Recent advances involving the use of carbon dioxide have attracted extensive attention due to environmental concerns and use of this potential carbon resource [1–8]. As a kind of potential approach, one of the most promising areas of carbon dioxide utilization is its application as a direct material for polymer synthesis. Poly(propylene carbonate) (PPC) is a highly alternating copolymer based on carbon dioxide and propylene oxide (PO), its structure is depicted in Scheme 1 [5,9–19].

PPC is a weak polar hydrophobic polymer with weak molecular chain interaction, and the existence of many weak polar, flexible C–O–C bonds in the backbone leads to its amorphous state, which is totally different from crystallizable polypropylene or polyethylene. Though transparent film having low gas permeability can be made from PPC [20–22], its dimension stability is poor even at 40 °C, which greatly limits its processing, storage as well as practical application. Therefore, enhancing molecular chain interaction of PPC is badly needed, and one possible way is to raise its molecular weight.

Molecular weight of PPC is a long term concern since the pioneering work of Inoue [5], even though the data are not always satisfactory in the literature. Inoue employed various kinds of dihydric compounds, including H_2O, resorcinol, dicarboxylic acids, and primary amines, combined with $ZnEt_2$ for the copolymerization of PO and CO_2. These



$$\left[\left(CH_2\text{-}\underset{CH_3}{CH}-O-\overset{\overset{O}{\|}}{C}-O\right)_x\left(CH_2\text{-}\underset{CH_3}{CH}-O\right)_{1-x}\right]_n \quad (x \geq 0.95)$$

Scheme 1. Chemical structure of poly(propylene carbonate).

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* Corresponding author. State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Renming Street 5625, Changchun, Jilin 130022, PR China. Tel.: +86 431 5262250; fax: +86 431 5689095.
E-mail address: xhwang@ciac.jl.cn (X. Wang).

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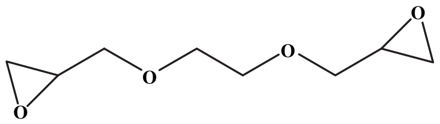
heterogeneous catalysts produced PPC with number average molecular weight (M_n) ranging from 30 to 150 kg/mol [5]. Following Inoue's discoveries, Kuran developed a copolymerization system using $ZnEt_2$ and pyrogallol, which produced PPC with M_n of 189 kg/mol [9]. However, the catalytic activities mentioned above were less than 30 g/(mol Zn h), and the reaction time was quite long (>40 h) [5,9]. Employing $Y(P_{204})_3$–$Al(i\text{-}Bu)_3$–glycerine catalyst, Shen carried out the copolymerization of CO_2 and PO under mild conditions to yield high molecular weight copolymer [10], but the carbonate unit content in the copolymer was much lower than that in common alternating PPC. Recently, the preparation of PPC with M_n higher than 140 kg/mol has been achieved using zinc glutarate catalyst, however, the copolymerization was carried out for 40 h [12a]. Subsequently, PPC with M_n up to 120 kg/mol was obtained employing rare-earth compounds/organic zinc/polylol ternary catalyst, and PPC with M_n higher than that value must be obtained under relatively lower copolymerization temperature (<60 °C) and longer reaction time (>35 h) [11,13b]. In addition there have been a variety of homogeneous catalysts for PO and CO_2 copolymerization. Aluminum porphyrin, serving as excellent catalyst for living polymerization, gave monodisperse PPC having a narrow PDI, while its M_n was only 3.9 kg/mol [15]. More recently, high activity and stereo-selective catalysts, such as β-diiminate zinc or salen-type catalysts, have been disclosed [16–20], but these catalysts often give low molecular weight PPC. Difunctional reagents, having ability to form networks, may raise molecular weight of polymer by means of chain extension like polyester [23,24], however, few reports are found for PPC.

The aim of this paper is to report a convenient and efficient way to synthesize PPC with M_n higher than 200 kg/mol, by adding a small amount of difunctional epoxides either to $Y(CCl_3OO)_3$–$ZnEt_2$–glycerine coordination catalysts or to PO and CO_2 copolymerization system, and PPC obtained in this way possesses improved thermal and mechanical performances.

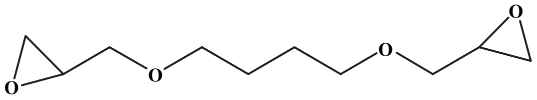
2. Experimental

2.1. Materials

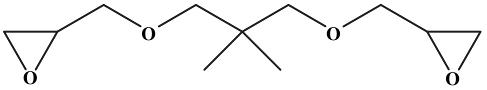
Ethylene glycol diethyl ether (EGDE), 1,4-butylene glycol diethyl ether (BUDE), neopentyl glycol diethyl ether (NPGDE) and 1,3-butadiene diepoxide (BDE) were distilled twice under argon and stored over 4 Å molecular sieves. Scheme 2 shows the chemical structures of these diepoxides. Propylene oxide (PO) and 1,3-dioxane were dried over calcium hydride and distilled prior to use. Glycerine was of analytical purity and distilled under reduced pressure prior to use. Yttrium trichloroacetate ($Y(CCl_3OO)_3$) and diethylzinc ($ZnEt_2$) were synthesized according to literature [25,26]. Commercial carbon dioxide (99.99% purity) was used without further purification.



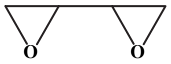
Ethylene glycol diethyl ether (EGDE)



1,4-Butanediol diglycidyl ether (BUDE)



Neopentyl glycol diglycidyl ether (NPGDE)



1,3-Butadiene diepoxide (BDE)

Scheme 2. Chemical structures of the diepoxides used for the terpolymerization with PO and CO_2.

2.2. Preparation and purification of copolymers

The $Y(CCl_3OO)_3$–$ZnEt_2$–glycerine coordination catalysts were prepared under argon atmosphere according to literature [13]. Calculated amount of catalyst and diepoxide was added into a two-necked flask under carbon dioxide protection at room temperature. After stirring at 60 °C for 2 h, the freshly produced catalyst suspension and calculated amount of PO were introduced into a 500 ml autoclave free of oxygen and water. Carbon dioxide was pressurized till 4 MPa. The reaction was carried out for 8 h at 65 °C, and then terminated by addition of methanol solution containing 5% dilute hydrochloric acid. The crude copolymer was dissolved in CH_2Cl_2, precipitated with methanol and dried at 40 °C under vacuum till constant weight.

2.3. Measurements

^1H NMR spectra of the copolymers were recorded at room temperature on a Bruker AV-300 NMR spectrometer using tetramethylsilane as internal reference. The carbonate or ether unit content in the copolymer was calculated from ^1H NMR spectra according to literature [5a,10]. The molecular weight and polydispersity of the copolymer were determined on a Waters 410 gel permeation chromatography at 35 °C in polystyrene standard using tetrahydrofuran as eluent. Intrinsic viscosity was measured in benzene at 35 °C using Ubbelohde viscometer. The thermal decomposition temperature was measured on a thermogravimetric analyzer (Model: Perkin–Elmer 7) under nitrogen atmosphere. Dynamic mechanical thermal analysis (DMTA) was performed on dynamic mechanical thermal analyzer V (Rheometric Scientific, Inc.) in a tension mode at a heating rate of 3 °C/min and a frequency of 1 Hz.

3. Results and discussion

3.1. Synthesis of PPC with high molecular weight

Copolymerization of CO_2 and propylene oxide (PO) using $Y(CCl_3OO)_3$–$ZnEt_2$–glycerine coordination catalyst generally produced common PPC with number average molecular weight (M_n) ranging between 50 and 100 kg/mol [13]. As listed in Table 1, when equimolar diepoxide and $ZnEt_2$ were added to the $Y(CCl_3OO)_3$–$ZnEt_2$–glycerine coordination catalyst during the catalyst preparation process, higher molecular weight of PPC was obtained. Addition of ethylene glycol diglycidyl ether (EGDE), 1,4-butanediol diglycidyl ether (BUDE) and neopentyl glycol diglycidyl ether (NPGDE) produced PPC with M_n higher than 200 kg/mol, which was approximately twice as much as that of common PPC.

M_n could also be determined from intrinsic viscosity by using the following equation [5d]:

$$[\eta]\ (\mathrm{dl/g}) = 1.11 \times 10^{-4} \bar{M}_n^{0.80}$$

As can be seen in Table 1, the M_n from the viscometric method was consistent with the GPC results, confirming that PPC with M_n value higher than 200 kg/mol was indeed achieved. It should be noted that a 50% decrease in yield was observed upon addition of diepoxides (Table 1), the reason will be discussed in the appropriate context.

Since EGDE, BUDE and NPGDE are diglycidyl ethers with similar structure, EGDE was chosen for the following study. Table 2 shows the dependence of M_n and polydispersity on the molar ratio of EGDE to $ZnEt_2$. Maximum M_n value and the narrowest molecular weight distribution (MWD) were obtained when equimolar of EGDE and $ZnEt_2$ was employed. When 0.5 equivalents of EGDE was added, the M_n value decreased by over 45%, whereas an increase beyond 1 equivalent also led to the decrease in M_n value along with a slight increase in the polydispersity (Table 2).

Table 1
Copolymerization of CO_2 and propylene oxide (PO) in the presence of diepoxide

Run	Diepoxide	Molar ratio of diepoxide to $ZnEt_2$[a]	Yield (g/(mol Zn h))	$M_n \times 10^{-4}$ (g/mol)		M_w/M_n[b]	CU[c] (%)
				GPC	Viscometer		
1[d]	–	0	543	10.9	10.3	2.9	97.8
2	EGDE	1	259	22.4	21.0	3.3	96.7
3	BUDE	1	285	23.2	22.0	3.6	97.3
4	NPDGE	1	274	21.0	20.5	3.2	98.1
5[e]	EGDE	1	167	22.7	19.9	3.4	97.5
6	BDE	1	279	12.5	10.4	3.7	98.5

Polymerization conditions: P_{CO_2}: 4 MPa; reaction time: 8 h; temperature: 65 °C. PO: 200 ml. The molar ratio of Zn:glycerine:Y was 20:10:1; $ZnEt_2$: 1.88 ml.

[a] Diepoxide was charged into catalyst.

[b] Determined by GPC.

[c] Determined by means of ^1H NMR analysis.

[d] Absence of diepoxide.

[e] PO: 80 ml.

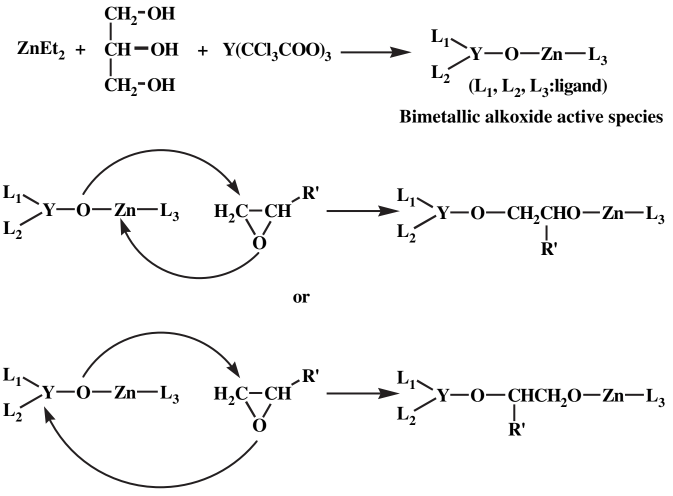
Table 2
Influence of the molar ratio of EGDE to $ZnEt_2$ on M_n and M_w/M_n

$EGDE/ZnEt_2$ (mol/mol)	M_n[a] $\times 10^{-4}$ (g/mol)	M_w/M_n[a]
0.5	12.1	3.7
0.75	14.0	4.2
0.9	19.0	5.4
1.0	22.7	3.3
1.1	19.6	4.0
1.25	14.6	3.8

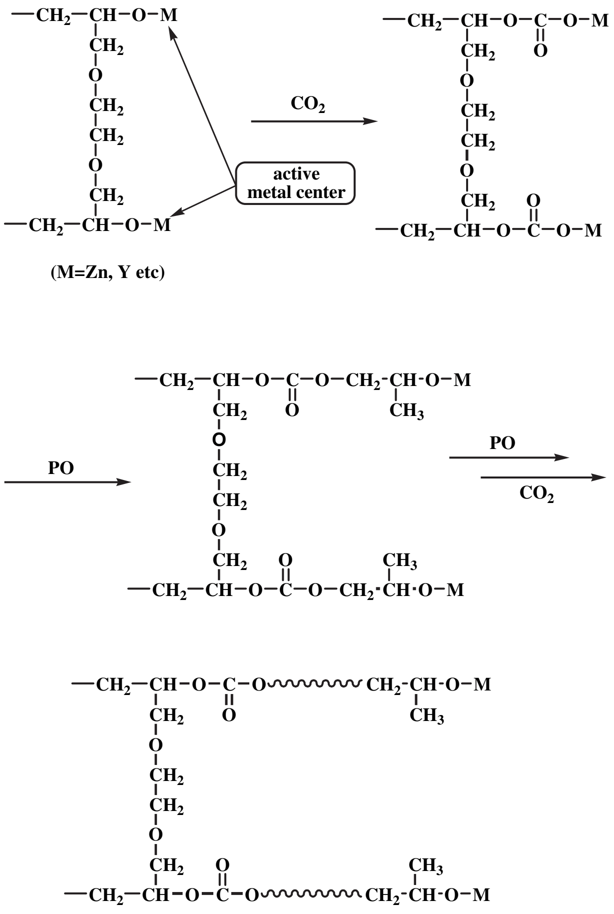
[a] Determined by GPC.

3.2. Possible double propagation mechanism

Although the active center of rare-earth complex/diethylzinc/glycerine system is still not very clear due to the complicated heterogeneous system, Shen and Tan had pointed out that a bimetallic active center between rare-earth metal and the reaction product between diethylzinc and glycerine was formed in the catalyst preparation step [10,11]. As shown in Scheme 3, both zinc alkoxide and yttrium alkoxide have the ability to initiate epoxide or carbon dioxide and thus catalyze the alternating copolymerization of carbon dioxide and epoxide. The introduction of yttrium trichloroacetate can significantly raise the copolymer yield as well as improve the molecular weight of the copolymer [13a]. Based on the fact that M_n value of PPC was doubled when equimolar $ZnEt_2$ and diepoxide were used considering metal alkoxide (zinc alkoxide and yttrium alkoxide) to be the active center in the catalyst system, a double propagation mechanism for the copolymerization of PO with CO_2 in the presence of diepoxide was proposed and is shown in Scheme 4. By nucleophilic attack of metal alkoxide on diepoxide, a new double propagation active species was generated in situ, and the copolymerization of PO and CO_2 proceeded simultaneously at both ends of



Scheme 3. The formation of bimetallic alkoxide active species and the interaction mode of active species with the epoxide.



Scheme 4. Double propagation mechanism for the copolymerization of propylene oxide with CO_2.

double propagation active species by a coordination–insertion mechanism [9b,16b]. The insertion of CO_2 into double propagation metal alkoxide was followed by insertion of PO into metal carbonate. If 1 equivalent of diepoxide to $ZnEt_2$ was applied, copolymerization was initiated by double propagation active species only, leading to doubled M_n value. When the ratio of diepoxide to $ZnEt_2$ was less than 1, coexistence of double propagation and single propagation active species reduced the M_n value, and broader MWD was obtained. When the ratio of diepoxide to $ZnEt_2$ was over 1, higher concentrations of diepoxide may cause chain transfer reactions leading to a decreased M_n value. The reason why redundant diepoxide causes chain transfer reactions was not clear at this moment. Possibly, diepoxide is more electron-donating and has stronger coordination ability to the catalyst than that of PO, higher concentrations of diepoxide may assist in the displacement of the growing chain and lead to an increased rate of chain transfer [17]. This double propagation model was different from that proposed by Inoue using aluminum porphyrins/ionic ammonium salt catalyst [15]. It was also different from Coates' model using Co^{III}(salen) complexes/phosphonium salt catalyst [16c], where the propagation proceeded on both sides of one metal center and the active species were in the middle of the polymer chain, polymers with M_n half of the theoretical values were formed after the dissociation or hydrolysis of metal center. In our work, two metal active species were connected by a diepoxide and the two active metal centers were located at both ends of a polymer chain separately, leading to the polymer with doubled M_n. Surprisingly, when the amount of PO decreased from 200 ml to 80 ml, the yield of the polymer decreased a lot, but the M_n value of PPC did not change significantly (Table 1, entries 2 and 5) [12a,27].

This model also suggests that the structure of diepoxide should influence the formation of double propagation active species. No significant M_n value increase was observed by the addition of 1 equivalent of 1,3-butadiene diepoxide (BDE) (Table 1, entry 6). The shorter distance between the two epoxide rings of BDE made the formation of double propagation active species more difficult because of steric effect.

When diepoxide was mixed with PO and charged into autoclave directly, as listed in Table 3, PPC with M_n around 200 kg/mol was also obtained at 1 equivalent of diepoxide to $ZnEt_2$. The formation of double propagation active species was further confirmed, probably due to the faster coordination rate of diepoxide with metal center than that of PO. The same reason may be true for the 50% yield decrease as shown in Table 1. Faster coordination of diepoxide severely inhibits PO binding and slows the rate of polymerization. Increasing the amount of diepoxide did not lead to crosslinked copolymer, on the contrary, it caused chain transfer reactions similar to the case where excess diepoxide was added to the catalyst during catalyst preparation process, and brought about a decreased M_n value of the resultant copolymer along with higher amounts of cyclic carbonates. The formation of cyclic carbonates also indicates the existence of chain transfer reactions [17], especially, the coupling of diepoxide and CO_2 gave copolymer with M_n value only 3.4 kg/mol in addition to 72% cyclic carbonates.

3.3. Thermal and mechanical properties

Mechanical property of PPC with different molecular weight was studied by DMA. As shown in Fig. 1, when M_n value increased from 109 to 227 kg/mol, the modulus of PPC below T_g increased from 4300 MPa to 6900 MPa. When the temperature was above T_g, PPC with M_n of 227 kg/mol showed modulus of 38 MPa, however, the modulus

Table 3
Terpolymerization of CO_2, propylene oxide (PO), and diepoxide

Run	Diepoxide	Molar ratio of diepoxide to $ZnEt_2$[a]	Yield (g/(mol Zn h))	$M_n \times 10^{-4}$ (g/mol)		M_w/M_n[b]	CU[c] (%)
				GPC	Viscometer		
1	EGDE	1	274	20.5	19.4	3.5	97.6
2	BUDE	1	278	19.9	19.0	3.2	98.5
3	NPDGE	1	387	19.2	18.7	3.7	96.4

For copolymerization conditions see Table 1.

[a] Diepoxide was mixed with PO and then charged into autoclave directly.

[b] Determined by GPC.

[c] Determined by means of ^1H NMR analysis.

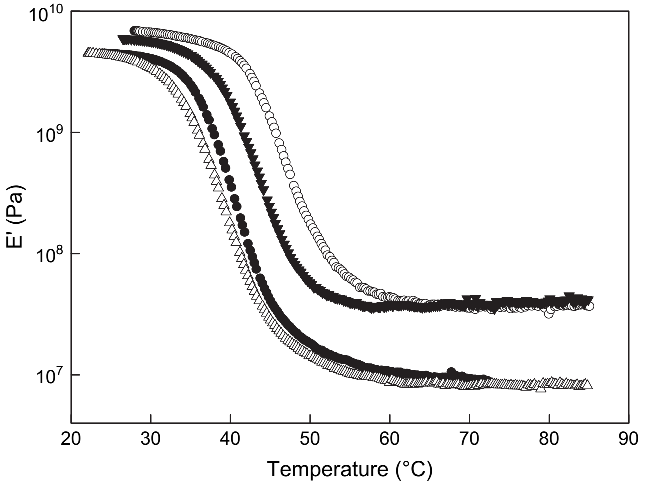


Fig. 1. Plots of storage modulus (E') against temperature of PPC with different M_n. ○, $M_n = 227$ kg/mol; ▼, $M_n = 156$ kg/mol; ●, $M_n = 109$ kg/mol; △, $M_n = 85$ kg/mol.

of PPC with M_n of 109 kg/mol was only 8.6 MPa. When the number average molecular weight increased from 109 to 227 kg/mol, a 37 °C increase of the onset degradation temperature was observed, and a modest increase of the glass transition temperature (6.1 °C) was also found (Figs. 2 and 3). Therefore, increasing the molecular weight of PPC may be one way to improve its thermal and mechanical performances.

4. Conclusions

A convenient way to synthesize PPC with number average molecular weight higher than 200 kg/mol was found by adding a small amount of difunctional epoxides either to $Y(CCl_3OO)_3$–$ZnEt_2$–glycerine coordination catalysts or to PO and CO_2 copolymerization system. The resultant PPC showed much improvement in the thermal and mechanical performances in comparison with ordinary PPC having lower M_n value.

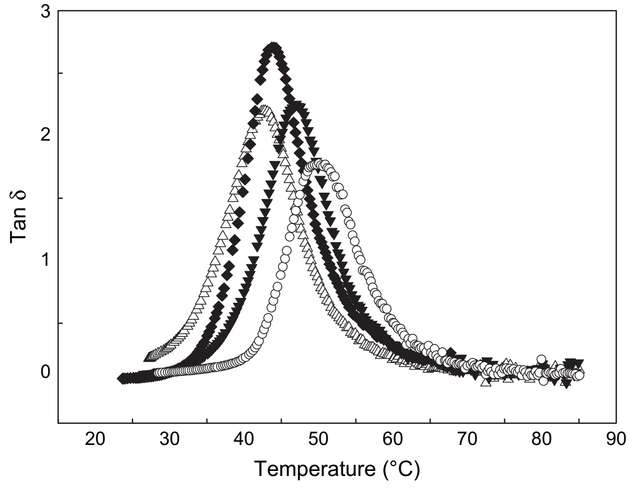


Fig. 2. Plots of tan δ against temperature for PPC with different M_n. ○, $M_n = 227$ kg/mol; ▼, $M_n = 156$ kg/mol; ◆, $M_n = 109$ kg/mol; △, $M_n = 85$ kg/mol.

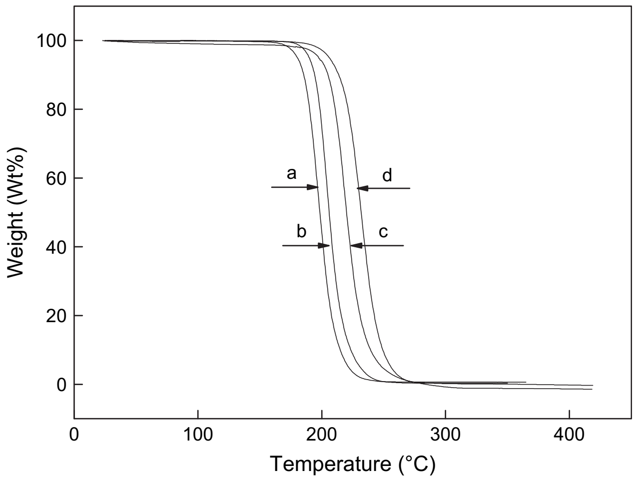


Fig. 3. TGA curves of PPC with various molecular weights. (a) $M_n = 109$ kg/mol; (b) $M_n = 132$ kg/mol; (c) $M_n = 156$ kg/mol; (d) $M_n = 227$ kg/mol.

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