Non-catalyst synthesis and thermal behaviors of three-arm star aliphatic polycarbonates

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ABSTRACT: Three-arm star aliphatic polycarbonates (TMP-PDTCs) were successfully synthesized via the ring-opening polymerization of 2,2-dimethyl trimethylene carbonate (DTC) initiated by trimethylolpropane (TMP) in the absence of catalysts. The structure of TMP-PDTCs was characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and gel permeation chromatography (GPC). The effects of reaction temperature, time, and the DTC/TMP molar feed ratio on the non-catalyst polymerization were investigated. The thermal behaviors of TMP-PDTCs were measured by differential scanning calorimetry (DSC). © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41998.

INTRODUCTION

Star polymers, consisting of multiple linear polymers attached to a central core, exhibit excellent properties as similar as dendritic polymers, e.g. globular structure, small hydrodynamic radius, low solution viscosity and crystallinity, high functionality and well-defined architecture.[1] However, the molecular structure and the synthesizing procedure of star polymers are simpler than those of dendritic polymers. Therefore, star polymers have attracted much attention in the biomedical fields.[1–3] Polylactide (PLA) and poly(ε-caprolactone) (PCL) are the most common biodegradable polymers, and the synthesis of star PLA or PCL and their further functionalization have been widely reported.[4–8]

Aliphatic polycarbonates are also one of the most important biodegradable polymers, which have the surface erosion degradation mechanism, the excellent biocompatibility and less acidic products in the course of degradation compared with PLA and PCL; so they are very suitable for biomedical materials.[9–11] Studies about aliphatic polycarbonates have been mainly focused on linear polymers during the past several decades. Moreover, linear aliphatic polycarbonates are usually synthesized by the ring-opening polymerization of cyclic carbonate monomer in the presence of metallic catalysts such as zincic, stannous or aluminous compounds.[12–17] These catalysts remain in materials to increase toxic side effects, which is unfavorable for biomaterials. Therefore, many researchers have been devoted to searching new methods without metallic catalysts to synthesize biodegradable aliphatic polycar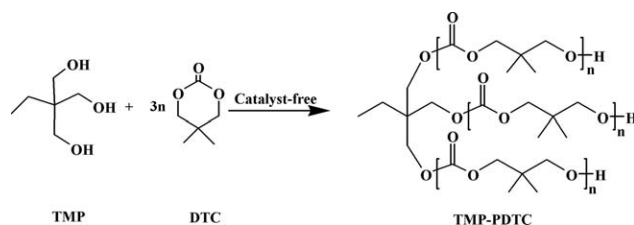bonates in recent years, such as enzyme-catalyzed polymerization,[18,19] catalyst-free polymerization in the presence of compounds containing hydroxyl or carboxyl group.[20–23] However, few studies on the catalyst-free polymerization for synthesizing star aliphatic polycarbonates have been reported.

In this article, the ring-opening polymerization of DTC was performed with TMP as the initiator and without any catalyst, and a kind of three-arm star aliphatic polycarbonates (TMP-PDTCs) was successfully synthesized. The effects of reaction conditions, such as temperature, time, and DTC/TMP molar feed ratio, on the catalyst-free polymerization were investigated. The thermal properties of TMP-PDTCs with different molecular weights were determined by DSC. The work provides a non-catalyst method to synthesize star biodegradable polycarbonates, which is very suitable for biomaterials.

EXPERIMENTAL

Materials

2,2-Dimethyl trimethylene carbonate (DTC) was synthesized as described in the literature,[24] recrystallized three times from ethyl acetate, and dried in vacuum before use (m.p.107–108°C). Ethyl acetate purchased from Tianjin Yongda Chemical Reagent Co. Ltd. was dried with anhydrous sodium carbonate overnight at room temperature and then distilled before use. Trimethylolpropane (TMP) was purchased from Tianjin Bodi Chemical Co. Ltd. and dried in vacuum before use. Stannous 2-ethylhexanoate [Sn(Oct)$_2$] was purchased from Shanghai Chemical Reagent Co. Ltd.. All other reagents were of AR grade and used as received.

Scheme 1. The synthetic route of TMP-PDTC.

Figure 1. FTIR spectra of TMP-PDTC (a) and LPDTC (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Synthesis of TMP-PDTC

TMP-PDTCs were synthesized from TMP and DTC in bulk without metal catalysts. The typical synthesizing procedure was as follows: a certain molar feed ratio of TMP and DTC was charged to a flask with a magnetic stirrer, and then the flask was sealed under reduced pressure. After the mixture was stirred at given temperature for a period of time, the polymerization was quenched by immersing the flask in cool water. The resulting product was dissolved in CH_2Cl_2 and precipitated with methanol. The precipitate was dried under vacuum at room temperature for 24 h. The obtained polymers were characterized by FTIR, NMR, and GPC.

For comparison, the ring-opening polymerization of DTC was carried out in the presence of TMP as the initiator and $Sn(Oct)_2$ as the catalyst. And the linear poly(2,2-dimethyl trimethylene carbonate) (LPDTC) was synthesized in the absence of TMP and $Sn(Oct)_2$.

Characterization

Melting point was determined on an X-4 microscope melting point apparatus. Fourier transform infrared (FTIR) spectra were recorded on a Vertex 70 spectrometer with a range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} by 32 scans. ^{1}H NMR and ^{13}C NMR spectra were measured on a Mercury VX-300 spectrometer and an Agilent 600 MHz DD2 spectrometer, respectively. Deuterated chloroform (CDCl$_3$) was used as solvent and tetramethylsilane (TMS) was used as internal standard. Number- and weight-average molecular weight (M_n and M_w) and polydispersity index (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) via Waters HPLC system equipped with a 2690D separation module and a 2410 refractive index detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 0.3 mL/min. Polystyrene standard with a narrow distribution was used to generate a calibration curve. Differential
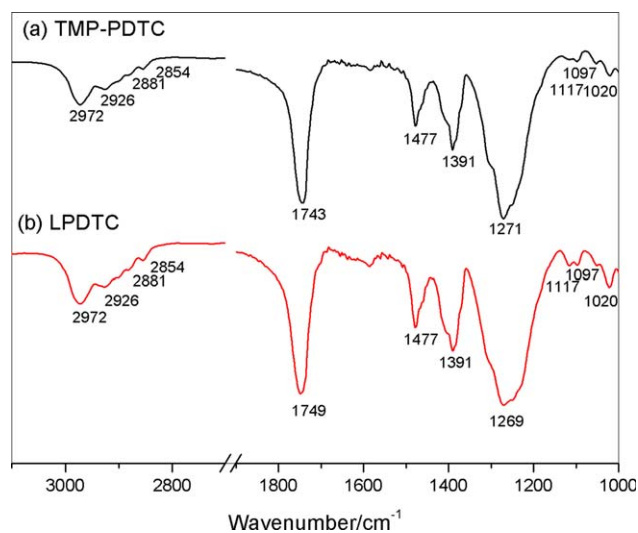
scanning calorimetry (DSC) was carried out on a NETZSCH DSC 200F instrument under nitrogen atmosphere. All samples were first heated from room temperature to 200°C at a heating rate of 10°C/min, then cooled to room temperature at a cooling rate of 10°C/min, and second heated to 200°C at 10°C/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of TMP-PDTC

The three-arm star polycarbonate (TMP-PDTC) was synthesized by the ring-opening polymerization of DTC using TMP with three hydroxyl groups as the initiator in the absence of catalysts. The synthetic route was shown in Scheme 1. The structure of TMP-PDTCs was characterized by FTIR, ^{1}H NMR, ^{13}C NMR, and GPC.

The FTIR spectrum of TMP-PDTC was presented in Figure 1, and the peak positions and their attributions were listed in Table I. The C═O and (O═)C─O stretching vibrations of DTC repeat units of TMP-PDTC appeared, which was similar to those of LPDTC. The ^{1}H NMR and ^{13}C NMR spectra of TMP-PDTC were shown in Figures 2 and 3, respectively. The proton signals and carbon signals of DTC repeat units and CH$_3$CH$_2$C(CH$_2$O)$_3$- group could be observed obviously. The

Table I. FTIR Peaks and Their Attributions for TMP-PDTC and LPDTC

| TMP-PDTC	LPDTC	Description for the bands observed	Ref.
2972	2972	C–H asymmetric stretching vibration for CH$_3$	25
2926	2926	C–H asymmetric stretching for CH$_2$	
2881	2881	C–H symmetric stretching for CH$_3$	
2854	2854	C–H symmetric stretching for CH$_2$	
1743	1749	C═O stretching vibration	26
1477	1477	C–H in plane bending vibration	
1391	1391	C–H symmetric bending vibration of CH$_3$	
1271	1269	(O═)C-O stretching vibration	26
1117, 1097, 1020	1117,1097,1020	C-O stretching vibration	
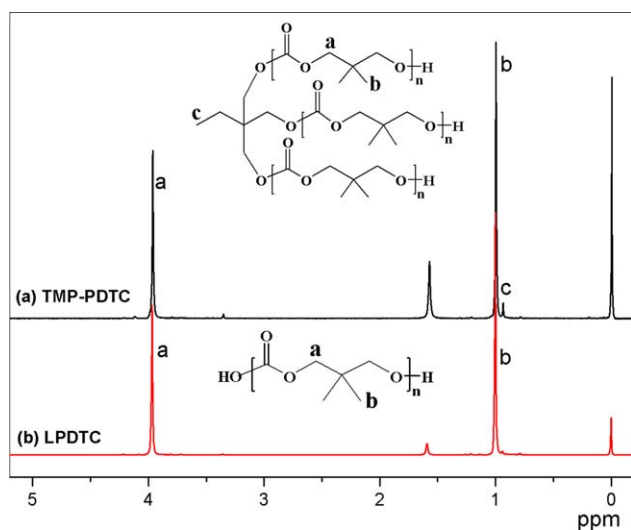
Figure 2. ^{1}H NMR spectra of TMP-PDTC (a) and LPDTC (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

number-average molecular weight and the polydispersity index of TMP-PDTC were measured by GPC. It could be seen from Figure 4 that the GPC curve of TMP-PDTC had a single peak, and that TMP-PDTC with moderate molecular weight was obtained. These characteristic results verified that the three-arm star polycarbonate (TMP-PDTC) could be successfully synthesized via the ring-opening polymerization of DTC initiated by TMP in the absence of catalysts.

In order to further demonstrate the feasibility of the non-catalyst polymerization of DTC initiated by TMP, the ring-opening polymerization without catalysts was compared with

that in the presence of Sn(Oct)$_2$ as the catalyst at 140°C for 6 h with the DTC/TMP molar feed ratio of 60. The molecular weight and the yield of TMP-PDTC synthesized in the presence of Sn(Oct)$_2$ as the catalyst were 13,200 g/mol and 84.7%, respectively. The molecular weight and the yield of TMP-PDTC prepared in the absence of catalysts were 10,380 g/mol and 77.7%, respectively. The results indicated that Sn(Oct)$_2$ could slightly accelerate the ring-opening polymerization of DTC, and that the molecular weight and the yield of TMP-PDTC obtained by the non-catalyst polymerization were comparable to those produced in the presence of Sn(Oct)$_2$ as the catalyst. Therefore, the non-catalyst polymerization was more suitable for the synthesis of biomedical polymers in consideration of bio-safety.

Influence of Reaction Temperature on the Ring-Opening Polymerization

When the ring-opening polymerization was carried out with the DTC/TMP molar feed ratio of 60 for 6 h, the effect of reaction temperature on the ring-opening polymerization was evaluated, and the results were listed in Table II from Samples 1 to 4. The polymer produced at 120°C could not be collected, probably because the product had lower molecular weight and could not be precipitated from methanol. When the temperature increased from 130°C to 140°C, both the $M_{n,GPC}$ and the yield of the resulting polymer increased gradually. The phenomena showed that the rate of the ring-opening polymerization increased with the increase of the reaction temperature. However, when the temperature was further raised to 150°C, the $M_{n,GPC}$ and the yield of TMP-PDTC decreased slightly. It was probably due to the fact that the thermal degradation happened at higher

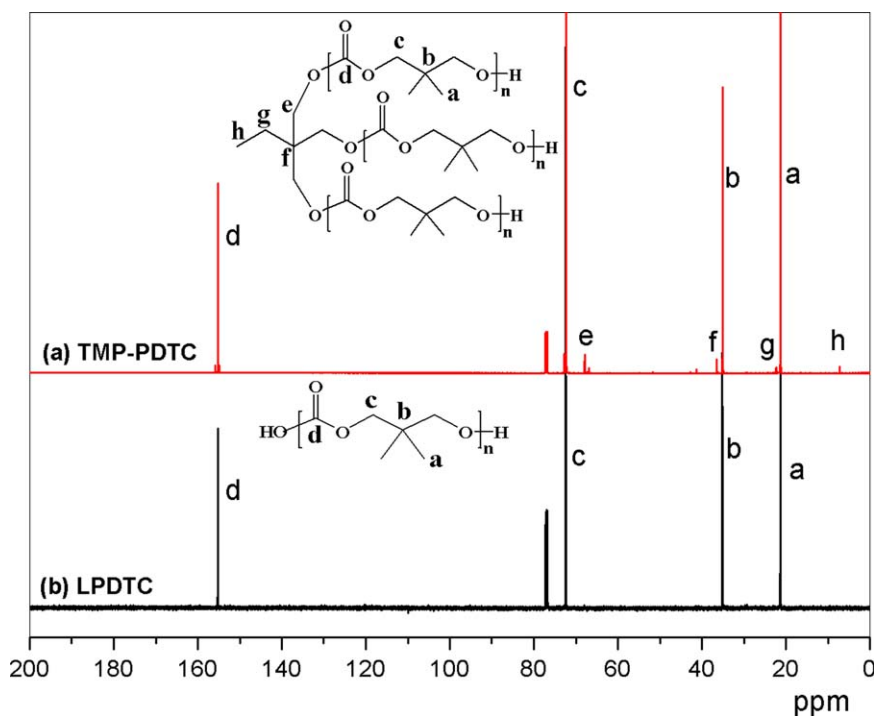**Figure 3.** ^{13}C NMR spectra of TMP-PDTC (a) and LPDTC (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
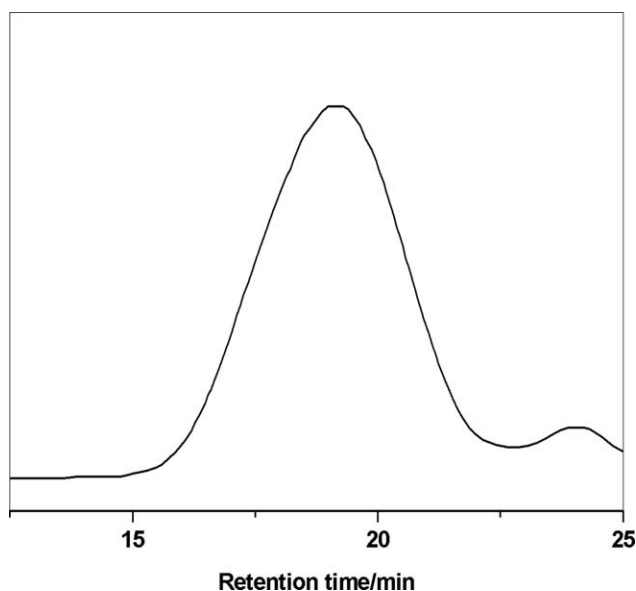
Figure 4. The typical GPC curve of TMP-PDTC.

temperature. The results demonstrated that the reaction temperature had a great effect on the ring-opening polymerization of DTC initiated by TMP in the absence of catalysts, and that TMP-PDTC with higher molecular weight and higher yield could be obtained at 140°C.

Influence of Reaction Time on the Ring-Opening Polymerization

The influence of reaction time on the ring-opening polymerization was studied at 140°C with the DTC/TMP molar feed ratio of 60. It could be found from Samples 3, 5, and 6 in Table II that with the elongation of reaction time from 6 to 12 h, the molecular weight of TMP-PDTC decreased, and that the yield also decreased obviously after 10 h. It probably resulted from the thermal degradation of the resultant polymer at higher temperature over a longer time. The result showed that TMP-PDTC with higher molecular weight and higher yield could be obtained at 140°C for 6 h.

Influence of DTC/TMP Feed Ratio on the Ring-Opening Polymerization

The effect of the DTC/TMP molar feed ratio on the molecular weight of the three-arm star polycarbonate was also investigated

Table II. The Effects of Temperature and Time on the Ring-Opening Polymerization Without Catalysts

Sample	T (°C)	Time (h)	n_{DTC}/n_{TMP}[a]	$M_{n,GPC}$[b]	M_w/M_n[b]	Yield/%
1	120	6	60	-	-	-
2	130	6	60	7854	2.31	70.3
3	140	6	60	10378	2.05	77.7
4	150	6	60	9684	1.79	56.5
5	140	10	60	9881	1.94	79.4
6	140	12	60	8903	2.07	69.6

[a] Molar feed ratio of DTC/TMP.
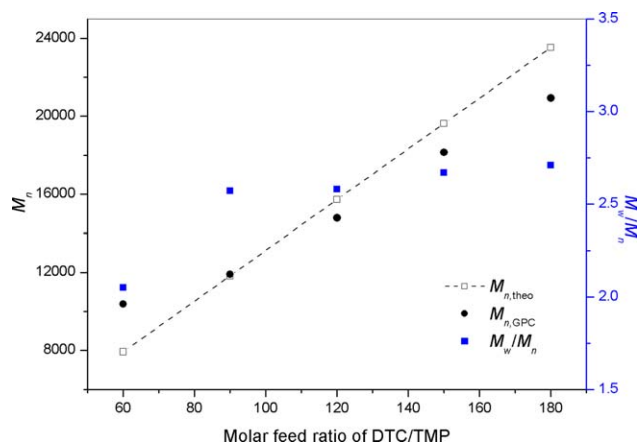[b] Data were obtained by GPC using THF as eluant and polystyrene as standard.

Figure 5. The plot of $M_{n,GPC}$, $M_{n,theo}$, and M_w/M_n of TMP-PDTC versus the DTC/TMP molar feed ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 140°C for 6 h with five DTC/TMP molar feed ratios: 60, 90, 120, 150, and 180, and the molecular weight of TMP-PDTC was determined by GPC. It could be observed from Figure 5 that the $M_{n,GPC}$ of TMP-PDTC increased gradually from 10,380 g/mol to 20,930 g/mol with the increase of the DTC/TMP molar feed ratio from 60 to 180. The result indicated that the molecular weight of TMP-PDTC could be effectively adjusted by changing the molar feed ratio of DTC/TMP. Meanwhile, $M_{n,GPC}$ had a little difference compared with the theoretical molecular weight ($M_{n,theo}$) which was calculated from the feed ratio. The hydrodynamic volume of TMP-PDTC was less than that of the linear polymer with the same molecular weight, so linear polystyrene used as standard probably resulted in some deviations.[5,27]

Thermal Behaviors

The melting and crystallization behaviors of TMP-PDTC were investigated by means of DSC. Figure 6 showed the DSC curves of
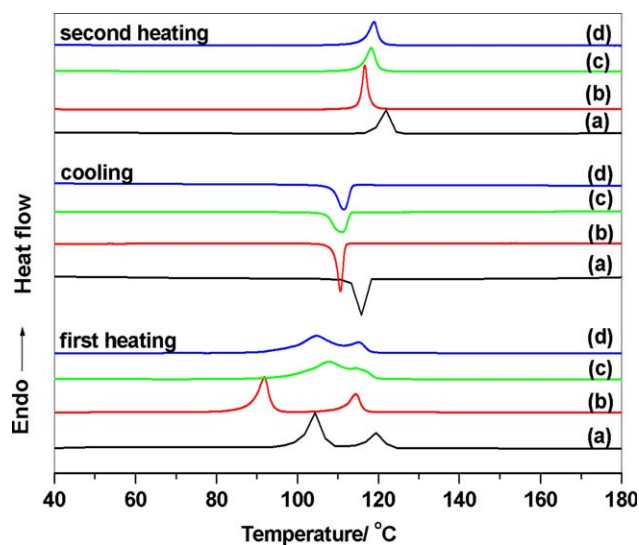

Figure 6. DSC curves of polycarbonates: (a) LPDTC; (b) TMP-PDTC60; (c) TMP-PDTC120; and (d) TMP-PDTC180. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. DSC Data of TMP-PDTC and LPDTC

| Sample | First heating | | Cooling T_c (°C) | Second heating T_m (°C) |
	$T_{m,1}$ (°C)	$T_{m,2}$ (°C)		
LPDTC[28]	104.3	119.5	115.9	121.9
TMP-PDTC60	91.8	114.4	110.6	116.6
TMP-PDTC120	107.9	115.1	111.0	118.2
TMP-PDTC180	104.7	115.1	111.5	119.0

TMP-PDTCs with different molecular weights in the first heating run, the cooling run and the second heating run; the DSC curves of the linear poly(2,2-dimethyl trimethylene carbonate) (LPDTC) were included for comparison; the characterization results were summarized in Table III. Three-arm star polycarbonates with the DTC/TMP molar feed ratio of 60, 120, and 180 were labeled to TMP-PDTC60, TMP-PDTC120, and TMP-PDTC180, respectively. For LPDTC, there were two transition peaks at the first heating, one peak at 104.3°C caused by the crystal transformation and the other peak at 119.5°C due to the crystal melting.[28] For TMP-PDTC60, TMP-PDTC120, and TMP-PDTC180, the two peaks appeared during the first heating, which implied that the crystal transformation and the crystal melting could also occur. LPDTC and TMP-PDTC had a monomodal crystallization peak in the cooling run, respectively; it showed that all samples could crystallize during cooling. In the second heating run for four samples, the crystal transformation peak disappeared and only one melting peak was observed. Furthermore, the melting point (T_m) and the crystallization temperature (T_c) of TMP-PDTC were apparently lower than those of LPDTC, and increased with the increase of the molecular weight of TMP-PDTC after the thermal history was erased. The results indicated that the macromolecular architecture had an effect on the thermal properties, and that the thermal properties could be varied by controlling the DTC/TMP molar feed ratio.

CONCLUSION

In this article, a series of three-arm star polycarbonates were successfully synthesized by the ring-opening polymerization of DTC initiated by TMP in the absence of catalysts. TMP-PDTC with higher molecular weight and higher yield could be obtained at 140°C for 6 h when the DTC/TMP molar feed ratio was 60. The molecular weight of TMP-PDTC could be effectively controlled by varying the DTC/TMP molar feed ratio. TMP-PDTC had crystallizability, and T_m and T_c increased with the increase of the molecular weight of TMP-PDTC.

ACKNOWLEDGMENTS

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