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Synthesis, characterization and ring-opening polymerization of a novel six-membered cyclic carbonate bearing pendent allyl ether group

Feng He*, Yan-Ping Wang, Gang Liu, Hua-Li Jia, Jun Feng, Ren-Xi Zhuo

Key Laboratory of Biomedical Polymers of the Ministry of Education, Department of Chemistry, Wuhan University, Wuhan 430072, China

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Abstract

A novel six-membered cyclic carbonate with pendent allyl ether group, 5-allyloxy-1,3-dioxan-2-one (ATMC), was synthesized from glycerol, and the corresponding polycarbonate, poly(5-allyloxy-1,3-dioxan-2-one) (PATMC) was further synthesized by ring-opening polymerization in bulk at 120 °C. Two kinds of catalyst, tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) and immobilized *porcine pancreas lipase* on silica particles (IPPL), were employed to perform the polymerization. The structures of the novel monomer and the resulting functional polymers were confirmed by FTIR, ^1H NMR, ^{13}C NMR, GPC and DSC. The molecular weight (M_n) of PATMC decreased rapidly with the increase of IPPL or $Sn(Oct)_2$ concentration. The highest molecular weight ($M_n = 48{,}700$ g/mol) of PATMC with the polydispersity of 1.31 was obtained at 0.1 wt% concentration of IPPL for 48 h. Postpolymerization oxidation reactions to epoxidize the unsaturated bonds of the PATMC were also achieved. The epoxide-containing polymers could afford facilities for further modification.

Keywords: Enzymatic ring-opening polymerization; Poly(5-allyloxy-1,3-dioxan-2-one); Allyl ether group

1. Introduction

Well-defined biodegradable polymers may be used for a variety of biomedical applications such as devices for controlled drug release, suture filaments, artificial skin, bioresorbable prostheses, ligature clamps, and bone fixation plates. Biodegradable polycarbonate forms one class of polymer that can be used for these applications [1]. Several kinds of aliphatic polycarbonates and their copolymers have been extensively investigated, such as poly(1,3-dioxan-2-one), poly(5,5-dimethyl-1,3-dioxan-2-one) and poly(lactide-*co*-1,3-dioxan-2-one) [2–4]. However, the rather low hydrophilicity and hydrodegradability of polymers introduced by the carbonate groups in the polymer chains decrease their compatibility with soft tissues and lower their biodegradability [5]. On the other hand, a number of applications in biomedical materials will greatly benefit from further research on biodegradable polymers that have various side groups. By careful design, these functional groups can be used to regulate hydrophilicity/hydrophobicity, permeability, bioresorption and mechanical properties [6]. Moreover, the pendent functional groups can facilitate covalent pro-drug attachment as well as other modifications. Recently, many polycarbonates with functional groups have been synthesized, such as carboxyl [7], hydroxyl [8], amino [9], vinyl [10,11], benzyl [12], etc. The synthesis of novel cyclic monomers containing a variety of functionalities has become an important method for the development of new biodegradable polymer materials with special properties for different applications.

Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) is the most often used chemical catalyst for the polymerization of lactones and cyclic carbonates, and has been approved for surgical and pharmacological applications by the FDA. However, it has been reported that $Sn(Oct)_2$ cannot be removed by a purification process such as the dissolution/precipitation method; thus, the residual Sn may be concentrated within matrix remnants after hydrolytic degradation [13]. Recently, research on enzymatic polymerization has received increasing attention as a new

* Corresponding author.
E-mail address: fenghe2002@hotmail.com (F. He).

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environmental friendly method of polymer synthesis, in contrast to chemical methods, which generally need harsh conditions and metallic catalysts that must be completely removed especially for medical applications. Up to now, various kinds of biodegradable polymers have been synthesized by enzymatic ring-opening polymerization, such as polyesters [14] and polycarbonates [7,15]. In our previous studies, we have reported that immobilized *porcine pancreas lipase* on silica particles (IPPL) can effectively catalyze the ring-opening (co)-polymerization of different six-membered cyclic carbonates [16,17].

The synthesis of a six-membered cyclic carbonate with allyl ester group, 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one (MAC) has been reported [11]. However, it is interesting that only one data about the homopolymerization of MAC were reported, while the polymerization of MAC was conducted without initiator or catalyst at 40 °C for 20 min. Although we attempted to synthesize homopolymers of MAC using chemical as well as enzyme catalysts, only insoluble products could be obtained even at low temperature (below 60 °C). It is probably due to high reactivity of the ester bond which resulted in the uncontrollability with the occurrence of transesterification side reaction during the polymerization. Considering the attractive versatility of allyl groups, we preliminarily designed another six-membered cyclic carbonate, 5-allyloxy-1,3-dioxan-2-one (ATMC) [18]. The allyl group of ATMC was connected to the cyclic carbonate by the relatively stable ether bond, and the linear homopolymers of ATMC were expected to obtain in control. The present paper reported in detail the synthesis and characterization of ATMC monomer and its polymers. IPPL-catalyzed polymerization was investigated in bulk, while $Sn(Oct)_2$ was also used as a well-known chemical catalyst for comparison. Furthermore, postpolymerization oxidation reactions were carried out with *m*-chloroperoxybenzoic acid to afford polymers with epoxide groups along the backbone. The further functionality of the epoxide groups can result in various polymer materials with different properties to meet different application needs.

2. Experimental

2.1. Materials

Allyl bromide was purchased from Acros Co. and used without further purification. *m*-Chloroperoxybenzoic acid (*m*CPBA) was purchased from Aldrich. Antipyrine was purchased form Shanghai Chemical Reagent Co., and recrystallized from benzene. $Sn(Oct)_2$ purchased from Aldrich Chemical Co. was purified by distillation under reduced pressure and dissolved in dry toluene (0.05 g/mL). IPPL was prepared according to Ref. [16]. Tetrahydrofuran (THF) and toluene were both dried over sodium–potassium alloy and distilled before use. Glycerol, benzaldehyde, *p*-toulenesulfonic acid, triphosgene, ethyl chloroformate and sodium hydride were analytical reagents and used as received.

2.2. Characterization

IR spectra were recorded on a Perkin–Elmer-2 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury VX-300 spectrometer using tetramethylsilane (TMS) as an internal reference and chloroform-*d* ($CDCl_3$) as a solvent. The molecular weights of polymers were measured by gel-permeation chromatography (GPC). GPC analysis was performed on a Agilent 1100 HPLC system equipped with a RI detector. *N*,*N*-Dimethylformamide was used as eluent at a flow-rate of 1.0 mL/min. Sample solutions (20 μL, 1.0% (w/v)) were injected for each analysis. Calibration was accomplished with narrow molecular weight distribution polystyrene standards (Polysciences, USA). DSC thermograms were registered with a Perkin–Elmer instrument Pyris-1 operator at 20 °C/min heating rate.

2.3. Synthesis of 5-hydroxy-1,3-benzylideneglycerol

5-Hydroxy-1,3-benzylideneglycerol was synthesized according to Ref. [12]. After two crystallizations from diethyl ether, white and silky needles were obtained: yield 40%; mp 80 °C. The NMR data were consistent with that reported previously.

2.4. Synthesis of 5-allyloxy-1,3-benzylideneglycerol

Sodium hydride (5.48 g, 0.16 mol) was added into a 250 mL round-bottom flask containing 150 mL of dried THF. The mixture was stirred vigorously at 0 °C for a while. 5-Hydroxy-1,3-benzylideneglycerol (18.00 g, 0.10 mol) was added to the mixture in batches. After 30 min, allyl bromide (12.10 mL, 0.14 mol) was added to the mixture dropwise. The reaction mixture was stirred at room temperature overnight. After precipitated NaBr was filtered off, the filtrate was decolorized by stirring with activated carbon and then filtered. Removal of the organic solvent *in vacuo* afforded the crude product. After two further recrystallization from ether and petroleum ether, white crystals were obtained: yield 20.30 g (92%); mp 50 °C.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.3-7.2$ (m, 5H, $-C_6H_5$), 6.0–5.8 (m, 1H, $-CH{=}CH_2$), 5.5 (s, 1H, $(-CH_2O)_2CHC_6H_5$), 5.4–5.2 (m, 2H, $-CH{=}CH_2$), 4.2–4.0 (d, 2H, $-OCH_2CH{=}CH_2$), 3.8–3.6 (d, 4H, $(-CH_2O)_2CHC_6H_5$), 3.3 (s, 1H, $-OCH(CH_2O-)_2$). ^{13}C NMR ($CDCl_3$, ppm): $\delta =$ 137.8, 129.5, 125.9 (C_6H_5), 134.6 ($-CH{=}CH_2$), 117.5 ($-CH{=}CH_2$), 101.1 ($(-CH_2O)_2CHC_6H_5$), 77.1 ($-OCH(CH_2O-)_2$), 70.0 ($-OCH_2CH{=}CH_2$), 67.6 ($(-CH_2O)_2CHC_6H_5$). FTIR (KBr pellets, cm^{-1}): 1646 ($\nu_{C=C}$).

2.5. Synthesis of 2-allyloxy-1,3-propanediol

5-Allyloxy-1,3-benzylideneglycerol (22.00 g, 0.10 mol), 100 mL of methanol and 100 mL of 1 mol/L hydrochloric acid were added into a 500 mL round-bottom flask and stirred at room temperature for 2 h. The pH value of the mixture was adjusted to 7.0 by adding sodium hydroxide. The mixture was

concentrated and extracted with ethyl acetate. After dried over magnesium sulfate, the filtrate was concentrated under vacuum. Distillation of the residue gave 12.80 g (93%) of a clear viscous liquid.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.0-5.8$ (m, 1H, $-CH{=}CH_2$), 5.4–5.2 (m, 2H, $-CH{=}CH_2$), 4.1 (d, 2H, $-OCH_2CH{=}CH_2$), 3.8–3.6 (m, 4H, $(HOCH_2)_2CH-$), 3.6–3.5 (m, 1H, $(HOCH_2)_2CH-$), 2.8 (s, 2H, $(HOCH_2)_2CH-$). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 134.8$ ($-CH{=}CH_2$), 117.5 ($-CH{=}CH_2$), 79.8 ($(HOCH_2)_2CH-$), 70.2 ($-OCH_2CH{=}CH_2$), 61.6 ($(HOCH_2)_2CH-$). FTIR (KBr pellets, cm^{-1}): 3387 (ν_{O-H}), 2924 (ν_{C-H}), 1646 ($\nu_{C=C}$).

2.6. Synthesis of ATMC

2-Allyloxy-1,3-propanediol (13.20 g, 0.10 mol) and antipyrine (22.60 g, 0.12 mol) and 200 mL of THF were mixed in a 500 mL round-bottom flask. A solution of triphosgene (9.90 g, 0.033 mol) in 50 mL of THF was added dropwise at 50 °C and then stirred overnight. The reaction mixture was filtered and concentrated. The residue obtained was dissolved in 100 mL of chloroform and then washed with aqueous hydrochloric acid and an adequate amount of water. After removal of the solvent, the crude product was purified by column chromatography (eluent: ethyl acetate/petroleum ether) to obtain 7.80 g (50%) of colorless liquid.

^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.0-5.8$ (m, 1H, $-CH{=}CH_2$), 5.4–5.2 (m, 2H, $-CH{=}CH_2$), 4.5 (m, 4H, $-OCOOCH_2CH-$), 4.2–4.1 (d, 2H, $-OCH_2CH{=}CH_2$), 3.9 (m, 1H, $-OCH(CH_2O)_2$). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 148.1$ ($-O-CO-O-$), 133.8 ($-CH{=}CH_2$), 117.9 ($-CH{=}CH_2$), 70.0 ($-OCH_2CH{=}CH_2$), 69.6 ($-COOCH_2CH-$), 66.3 ($-OCH(CH_2O)_2$). FTIR (KBr pellets, cm^{-1}): 1741 ($\nu_{C=O}$), 1646 ($\nu_{C=C}$).

2.7. General procedure for the $Sn(Oct)_2$-catalyzed polymerization

All reactions were carried out in bulk at 120 °C. ATMC and the catalyst solution were transferred into a thoroughly dried glass flask with a magnetic stirring bar. The flask was degassed by several vacuum-purge cycles that also removed solvent introduced in the catalyst solution. The flask was then sealed *in vacuo* and immersed in an oil bath at 120 °C with stirring for a predetermined time. After the reaction was completed, the reaction mixture was dissolved in dichloromethane and then purified by reprecipitation for several times. The product was dried *in vacuo* at room temperature to constant weight.

2.8. General procedure for the IPPL-catalyzed polymerization

All reactions were also carried out in bulk at 120 °C. ATMC and IPPL were dried (40 Pa, 24 h, room temperature) with anhydrous phosphorus pentoxide as desiccant before use. The mixture of ATMC and IPPL was then transferred into a thoroughly dried glass flask with a magnetic stirring bar. Then the flask was evacuated, purged with N_2 three times, sealed and placed in an oil bath at 120 °C with stirring for a predetermined time. After the reaction was completed, the reaction mixture was dissolved in dichloromethane, and the insoluble immobilized enzyme was removed by filtration. Then the solvent was concentrated under reduced pressure to obtain the crude polymer, which was further purified by precipitation. Then the product was dried *in vacuo* at room temperature to constant weight.

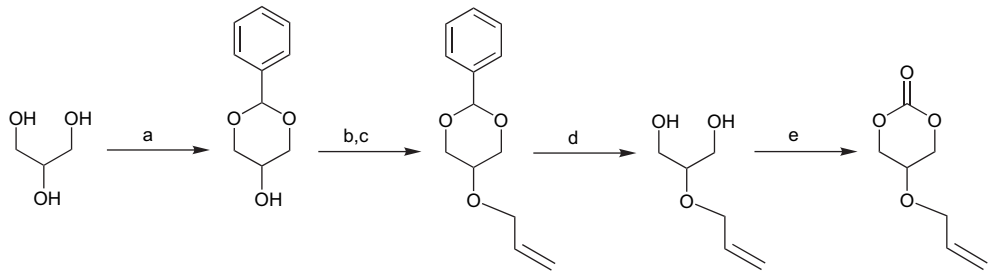
2.9. Epoxidation of the allyl groups of PATMC

In a typical reaction, 0.10 g of PATMC, 2–4 molar excess of *m*CPBA (70% maximum purity) with respect to the double bonds of ATMC and 5 mL of $CHCl_3$ were charged into a 20 mL round-bottom flask. The reaction mixture was refluxed for 12 h. Then the solution was filtered and precipitated into hexane. The polymer was dried for 24 h *in vacuo*.

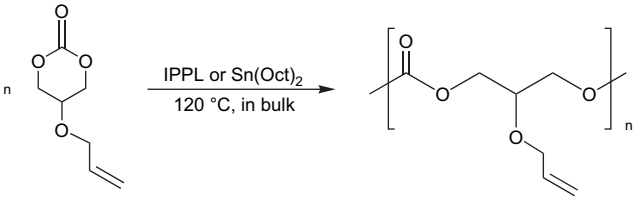
3. Results and discussion

3.1. Monomer synthesis

The general strategy applied for the synthesis of the novel functionalized carbonate monomer, ATMC, is shown in Scheme 1. 5-Hydroxy-1,3-benzylideneglycerol was prepared by the reaction of glycerol with benzaldehyde according to a literature procedure [12]. The subsequent allylation was conducted from the ionization of 5-hydroxy-1,3-benzylideneglycerol by a 1.6 equivalent of sodium hydride followed by the dropwise addition of 1.4 equivalent of allyl bromide to give 5-allyloxy-1,3-benzylideneglycerol. Then the deprotection of



Scheme 1. Synthesis of ATMC. Reaction conditions: (a) benzaldehyde, toluene, *p*-toulenesulfonic acid, reflux, 6 h; (b) sodium hydride, THF, 0 °C, 30 min; (c) allyl bromide, 25 °C, 12 h; (d) 1 mol/L HCl, methanol, 25 °C, 2 h; (e) triphosgene, antipyrine, THF, 50 °C, 12 h.



Scheme 2. Ring-opening Polymerization of ATMC.

the benzyl group of 5-allyloxy-1,3-benzylideneglycerol was achieved quantitatively in the mixture of 1 mol/L HCl aqueous solution with methanol at room temperature for 2 h. However, the formation of the final cyclic carbonate monomer was proved to be a failure when 2-allyloxy-1,3-propanediol was treated with the most commonly used reagent, ethyl chloroformate. By selecting a more reactive reagent triphosgene, the synthesis of ATMC was finally achieved with a moderate yield of 50%. The structure of the novel six-membered cyclic carbonate was confirmed by FTIR, ^{1}H NMR and ^{13}C NMR.

3.2. Polymer synthesis

Polymerization reactions were carried out at 120 °C in bulk using IPPL or $Sn(Oct)_2$ as the catalyst (shown in Scheme 2). The polymerization temperature was kept at 120 °C because ATMC could polymerize without crosslinking at that temperature. It was reported that the pure 1,3-dioxan-2-one (TMC) monomer could be spontaneously polymerized at 100 °C [19]. In fact, we also found that ATMC can be thermally oligomerized at 120 °C in this study. But both the M_n and yield of the oligomers were significantly lower than those of the polymers obtained by lipase-catalyzed and $Sn(Oct)_2$-catalyzed polymerizations. These results indicated that the lipase enzymes and $Sn(Oct)_2$ actually promoted the ring-opening polymerization.

The influences of reaction time and catalyst concentration on polymerization were investigated. The results are summarized in Table 1.

In the case of the IPPL-catalyzed polymerization, reaction times of 24 h, 48 h and 72 h were investigated at 120 °C.

Table 1
Ring-opening polymerization of ATMC catalyzed by IPPL and $Sn(Oct)_2$

Entry[a]	Catalyst	[M]/[I][b]	Time (h)	Yield (%)	M_n[c]	M_w/M_n[c]
1	IPPL	1000	24	64	39,600	1.36
2	IPPL	1000	48	79	48,700	1.31
3	IPPL	500	48	78	28,600	1.37
4	IPPL	200	48	73	14,300	1.54
5	$Sn(Oct)_2$	1000	24	77	30,700	1.38
6	$Sn(Oct)_2$	1000	48	21	22,000	1.26
7	$Sn(Oct)_2$	500	24	86	18,100	1.19
8	$Sn(Oct)_2$	200	24	70	16,400	1.07
9	$Sn(Oct)_2$	100	24	57	16,300	1.03

[a] Polymerization temperature: 120 °C.
[b] Molar ratio of monomer to catalyst when catalyzed by $Sn(Oct)_2$; weight ratio of monomer to catalyst when catalyzed by IPPL.
[c] Number- and weight-average molecular weight and polydispersity determined by GPC.

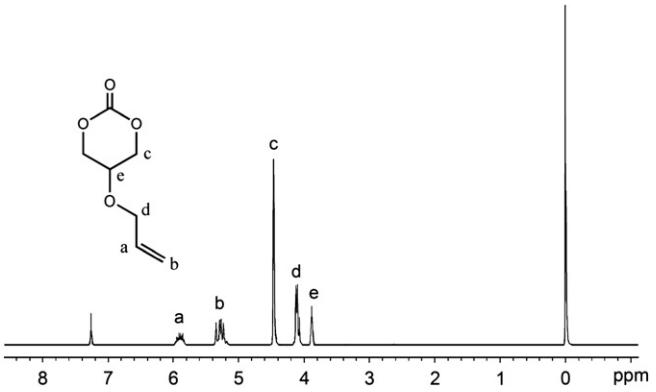


Fig. 1. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of ATMC.

However, only insoluble products can be obtained when the polymerization was carried out for 72 h. On the other hand, PATMC obtained by polymerization for 48 h has a higher molecular weight and reaction yield than that obtained by polymerization for 24 h. Furthermore, when the polymerization was catalyzed by IPPL at 120 °C for 48 h, the M_n of PATMC decreased rapidly from 48,700 to 14,300 g/mol with the increase of IPPL concentration from 0.1 to 0.5 wt%, while the yield also decreased slightly from 79% to 73%. The number of the initiating species increased with the increase of the enzyme concentration.

In the case of the $Sn(Oct)_2$-catalyzed polymerization, however, the effect of reaction time on the polymerization was quite different. With the increase of polymerization time from 24 h to 48 h, some insoluble products mixed with soluble products were obtained; thus the yield of PATMC was quite low. The occurrence of other side reaction during the polymeri zation could not be avoided with a longer reaction time at high temperature. Moreover, the catalyst concentration had also great influence on the polymerization in this system. Increasing the $Sn(Oct)_2$ concentration from 0.1 to 1.0 mol% resulted in the decrease of M_n from 30,700 to 16,300 g/mol. It seemed to show that the $Sn(Oct)_2$-catalyzed polymerization

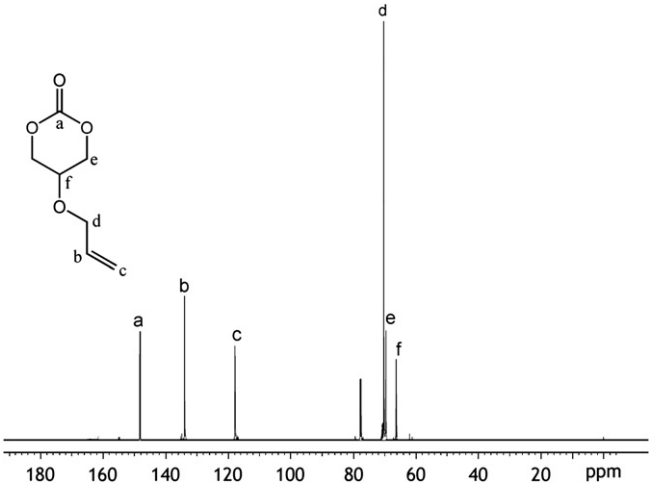


Fig. 2. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of ATMC.

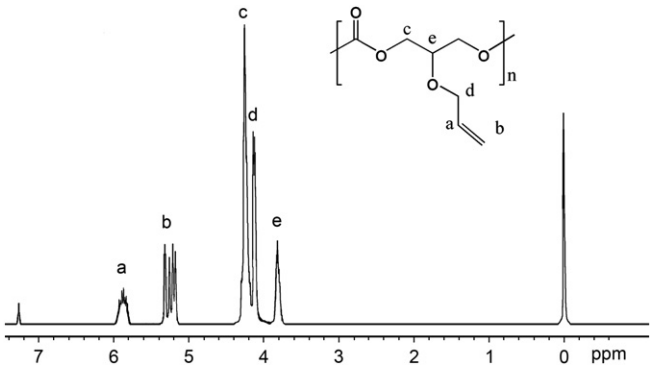


Fig. 3. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of PATMC.

had a higher reaction rate than the IPPL-catalyzed polymerization, while the little time reached to the reaction equilibrium was needed for the $Sn(Oct)_2$-catalyzed polymerization.

For all the polymers, GPC analysis showed unimodal distribution and polydispersities were in the range of 1.03–1.54. There was no peak in the zone of low molecular weights, thus indicating the absence of residual ATMC monomer.

3.3. Characterization

The structure of the novel functional cyclic carbonate as well as its polymers were confirmed by FTIR, ^{1}H NMR and ^{13}C NMR anlysis. IR spectra revealed the characteristic absorption bands of carbonyl group and double-group around 1741 cm^{-1} and 1646 cm^{-1} both in monomer and in polymers.

In the ^{1}H NMR spectrum of ATMC (Fig. 1), the characteristic peak areas of allyl group were observed from 6.0–5.8 ppm and 5.4–5.2 ppm. ^{13}C NMR spectrum of ATMC (Fig. 2) also showed the characteristic peaks of allyl group at 133.8 ppm and 117.9 ppm.

Deprotection was monitored by the disappearance of the phenyl protons (7.3–7.2 ppm) of the benzyl group and the appearance of hydroxy proton (2.8 ppm). When 2-allyloxy-1,3-propanediol was treated by D_2O, the peak of 2.8 ppm disappeared.

The data from NMR spectroscopy of PATMC are fully consistent with the anticipated chemical structure as compared to the spectrum of the monomer. The typical ^{1}H NMR and ^{13}C

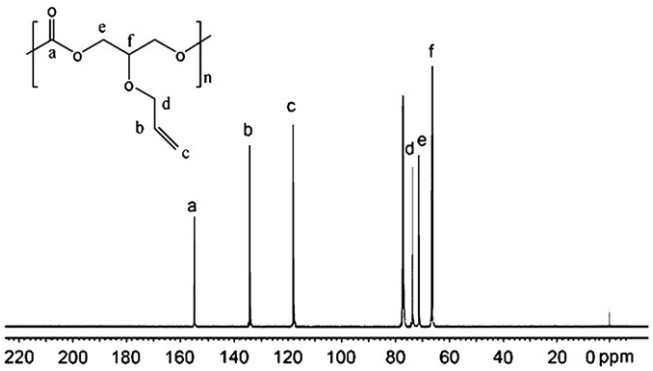
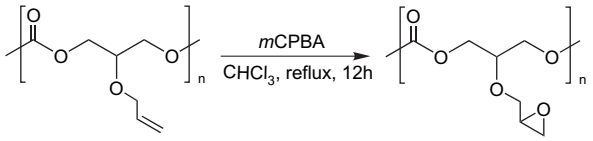


Fig. 4. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of PATMC.



Scheme 3. Epoxidation of PATMC by *m*CPBA.

NMR spectra of PATMC are shown in Figs. 3 and 4. Although the repeat units of PATMC contain stereogenic centers, neither proton signals in ^{1}H NMR nor carbon signals in the ^{13}C NMR spectrum showed obvious signals that might have resulted from differing stereochemical relationships between adjacent repeat units. In addition, ^{1}H NMR spectra of polycarbonate obtained offered no evidence for decarboxylation occurrence during the polymerization because no methylene protons of ether-linked repeat units ($-CH_2-O-CH_2-$) could be detected.

DSC was used to analyze the temperatures corresponding to polymer glass and melting transitions (T_g and T_m, respectively). The results showed that T_g of PATMC was around −40 °C and T_m was around 24 °C.

3.4. Epoxidation of the allyl groups of PATMC

Scheme 3 displays the synthetic strategy for epoxidizing the allyl groups of PATMC. The oxidation reactions were carried out in refluxing chloroform, and afforded almost complete epoxidation of the allyl groups within 12 h. Figs. 5 and 6 display the ^{1}H and ^{13}C NMR spectra of PATMC after epoxidation with *m*CPBA, respectively. The epoxidation reaction caused the disappearance of allyl proton signals (6.0–5.8 and 5.4–5.2 ppm) and the appearance of oxirane proton signals (3.2 and 2.8–2.6 ppm). The ^{13}C NMR spectrum also confirmed the disappearance of the olefinic carbons at chemical shifts of 133.8 and 117.9 ppm in comparison to that of PATMC, while the appearance of the two oxirane carbons at 44.2 and 50.8 ppm were observed.

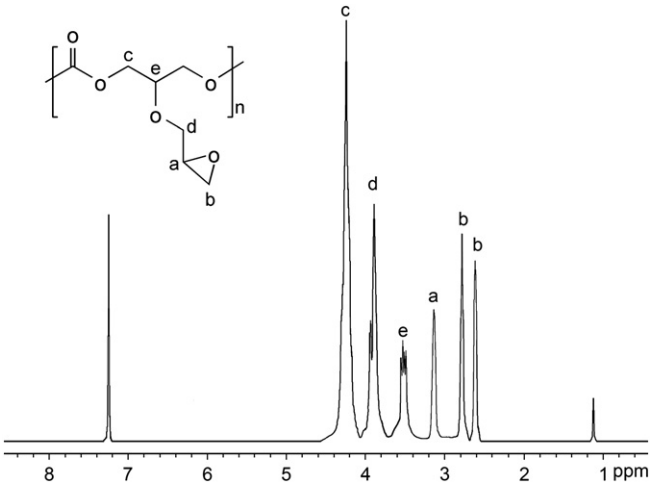


Fig. 5. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of PATMC after epoxidation of the double bonds.

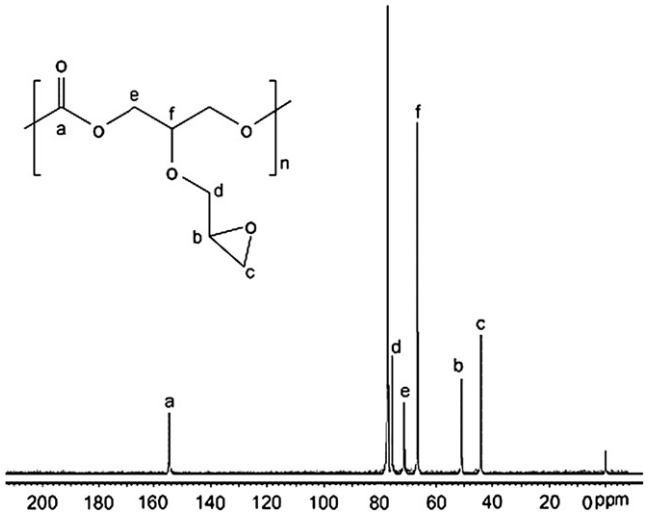


Fig. 6. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of PATMC after epoxidation of the double bonds.

Postpolymerization oxidation of the allyl groups of PATMC successfully introduced epoxide groups along the polymer chain. The epoxide groups could provide an effective approach to further modify the polymers reacted by many nucleophilic reagents, such as alcohols, amines, carboxyl acids, etc. These additional modifications can be used to adjust the properties of the polymer materials and also offer sites for crosslinking or possibly for drug-attachment/delivery applications.

4. Conclusions

The synthesis of a novel functional cyclic carbonate containing allyl ether groups, 5-allyloxy-1,3-dioxan-2-one (ATMC) was reported. Ring-opening polymerization of ATMC was carried out in bulk at 120 °C using chemical and enzyme catalysts (IPPL and $Sn(Oct)_2$). As expected, cyclic carbonate monomer with allyl groups connected by ether bond could result in targeted linear polymers without crosslinking. The highest molecular weight ($M_n = 48{,}700$ g/mol) of PATMC was obtained at 0.1 wt% concentration of IPPL for 48 h. Postpolymerization oxidation of PATMC was carried out in refluxing chloroform for 12 h. The allyl groups can be almost completely epoxidated by *m*CPBA. Physical and biodegradable evaluations of PATMC as well as the further functionality of epoxide groups are currently underway in our laboratory.

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