

## Syntheses of Cyclic Poly(lactones) by Zwitterionic Ring Opening Polymerization Catalyzed by N-Heterocyclic Carbene

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**ABSTRACT:** Synthesis of cyclic biopolymers from renewable monomers remains a big challenge because of lack of efficient catalysts. The organocatalyst of N-heterocyclic carbene (NHC), (+)-1-methyl-3-menthoxyethyl imidazol-2-ylidene, is used to prepare cyclic poly(lactones) including poly( $\epsilon$ -caprolactone) (poly( $\epsilon$ -CL)), poly( $\delta$ -valerolactone) (poly( $\delta$ -VL)), and poly( $\epsilon$ -caprolactone-co- $\delta$ -valerolactone) (poly( $\epsilon$ -CL-co- $\delta$ -VL)) via zwitterionic ring opening polymerization. The NHC catalyst is founded a highly efficient organic catalyst for the polymerization. The resulting cyclic polymers show a melting temperature ( $T_m$ ) in a range of 20–60°C, which is dramatically lower than the  $T_m$  of cyclic poly(lactide) ( $T_m = 120$ –150°C). The resulting copolymer, cyclic poly( $\epsilon$ -CL-co- $\delta$ -VL) owns high molecular weight comparing with corresponding linear poly( $\epsilon$ -CL-co- $\delta$ -VL) produced by other catalysts. The synthesized cyclic homo and copolymers were characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry–thermogravimetric analysis and matrix-assisted laser desorption ionization-time of flight mass spectrometry. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

Since the depletion of crude oil-based raw materials, the efficient use of renewable resources as feed stocks to produce biodegradable polymers such as poly(lactide) (PLA) and poly( $\epsilon$ -caprolactone) as well as their copolymers has been an increasingly important issue, which is attracting wide interest both in academia and industry.<sup>1–17</sup> Biodegradable polymers may find extensive applications in packaging, compost bags, agriculture, horticulture, medicine, and others.<sup>1–17</sup> However, most of the synthetic biodegradable polymers and copolymers are based on a long chain linear molecular architecture.<sup>1–17</sup> Because of unavailable efficient synthetic methods, very limited works were reported in terms of cyclic polymers from renewable monomers.<sup>18–25</sup> Cyclic polymer is one of the simplest topological isomers of linear structure.<sup>18–25</sup> Comparing with linear isomers, cyclic polymers own advantages of low-melting viscosity, controllable molecular weight, rapid crystallization towards a high degree of crystallinity and nonchemical emission during processing.<sup>18–25</sup> With all the unique properties, cyclic polymers may find specific applications in microelectronics, textiles, packages, biomedical and pharmaceutical industries as absorbable implant material and a vehicle for controlled drug delivery.<sup>18–25</sup> Further, the present advanced progress in analytical methodology enables

us to identify the detailed structure of a cyclic polymer. Therefore, developments in the exploration of biodegradable cyclic polymer are now of great interest from the view point of both unique properties and the component of interlocked materials. Comprehensive relationship of structural properties of cyclic biodegradable polymers may open a new door for their applications in many fields.

Cyclizing long chain is one of the challenges to synthesize cyclic polymers with a large macrocycle because of the formidable entropic inhibitions.<sup>26,27</sup> Two strategies are commonly used to prepare cyclic polymers from the  $\alpha$ ,  $\omega$ -difunctional linear precursors: (1) utilization of ring-chain equilibrium which occurs simultaneously in many ring opening polymerization (ROP) and polycondensation chain growth processes; (2) inter-/intra-molecular end-to-end cyclization.<sup>18–25</sup> Enzyme catalysts have been also employed to synthesize biodegradable cyclic polymers accompanying with linear isomers.<sup>28</sup> Because of the intrinsic limitations of above-mentioned synthetic methods, it is unavoidable to purify the cyclic polymer products from linear chain contamination. Unfortunately, all the reported purification processes are generally complex and highly cost.<sup>29–33</sup> Very recently, Waymouth and Hedrick's group has reported various organocatalysts such as N-heterocyclic carbenes (NHC) for the

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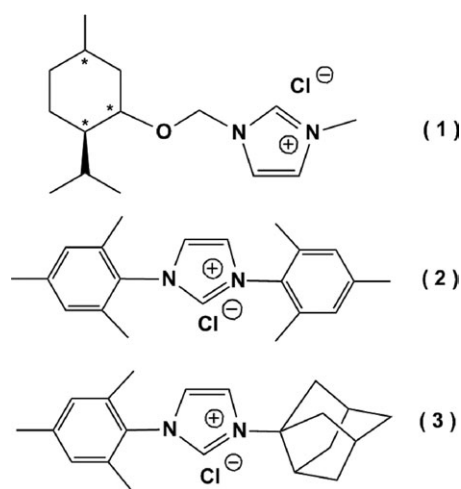


Figure 1. Catalyst precursors.

formation of both cyclic and linear biopolymers by zwitterionic ROP.<sup>34–39</sup> Unlike metal based catalysts, ROP catalyzed by the NHCs produce “green” cyclic polymers without any metal contamination caused by the trapped catalyst species.<sup>34–39</sup> In this respect, we developed a highly efficient NHC catalyst precursor (+)-1-methyl-3-menthoxyethyl imidazolium chloride (1) (Figure 1). Compound (1) could be conveniently prepared in large scale from commercially available chemicals comparing with the high-priced precursors (2) and (3) (Figure 1).<sup>34–40</sup> The NHC catalyst derived from precursor (1) displayed excellent activity towards ROP of L-lactide forming cyclic poly(L-lactides) with high  $M_w$  and narrow MWD.<sup>40</sup> In addition, the NHC catalyst was stable in the presence of air.<sup>40</sup> Herein, we report the preliminary results for the ROP of  $\epsilon$ -CL and  $\delta$ -VL to synthesize cyclic polymers and copolymers catalyzed by the NHC catalyst derived from precursor 1.

## EXPERIMENTAL

### General

All reactions and polymerizations were carried out in a M. Braun Glove box under argon atmosphere or standard Schlenk and vacuum line procedures.  $\epsilon$ -Caprolactone and  $\delta$ -valeurolactone were purchased from Sigma-Aldrich Chemicals and purified by distillation under reduced pressure before use. Catalyst precursor (+)-1-methyl-3-menthoxyethyl imidazolium chloride (1) was prepared according to literature.<sup>40</sup> Potassium *t*-butoxide was purchased from Merck Co. and used as received. Solvents diethyl ether, *n*-hexane, dichloromethane (DCM), tetrahydrofuran (THF) were purchased from JT Baker and purified by an Mbraun solvent purification system (SPS). Deuterated chloroform ( $\text{CDCl}_3$ ) was purchased from Cambridge Isotope Laboratories.

### Characterization

$^1\text{H}$ - and  $^{13}\text{C}$ -nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 400 MHz spectrometer and  $\text{CDCl}_3$  as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to tetramethylsilane and chloroform ( $^1\text{H}$  and  $^{13}\text{C}$ ). The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity indexes ( $M_w/M_n$ )

of the polymers were estimated using a gel permeation chromatography (GPC) system. The system was calibrated with polystyrene standards. Chromatographies were performed in THF (at a flow rate of 1.0 mL/min) on an Agilent 1200 Chromatograph equipped with a RI detector. A combination of  $2 \times \text{PLgel } 5\text{-}\mu\text{m}$  mixed-columns ( $M_w$  200– $3 \times 10^6$ ) was used.

Differential scanning calorimetry (DSC) was performed using a PerkinElmer Diamond DSC. It was calibrated using high purity indium at a heating rate of  $10^\circ\text{C}/\text{min}$ . DSC was performed from  $-50$  to  $80^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . Melting temperature ( $T_m$ ) was determined from the second heating scan.

Matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) measurements were obtained using Bruker Daltonics Autoflex TOF/TOF. Cyclic PCL was dissolved in THF (5 mg/mL) and 1- $\mu\text{L}$  solution, 20- $\mu\text{L}$  dithranol solution (15 mg/mL) was used as the matrix and 1- $\mu\text{L}$  sodium iodide (5 mg/mL) was added as the cation source.

### Synthesis of (+)-1-Methyl-3-menthoxyethyl imidazol-2-ylidene Catalyst from Precursor 1

In a glove box, (+)-1-methyl-3-menthoxyethyl imidazolium chloride (100 mg, 0.35 mmol) was added to a dry Schlenk flask equipped with a magnetic stirring bar, and 30-mL anhydrous THF was added. The precursor is sparingly soluble in THF. To this, 81.0 mg (0.69 mmol) of potassium *t*-butoxide was carefully added. After the addition of potassium *t*-butoxide the carbene precursor was completely soluble and the reaction mixture was stirred for 45 min to produce a light yellow color catalyst solution. The catalyst solution was filtered through a 45- $\mu\text{m}$  syringe filter to produce a clear carbene solution. The neat carbene solution was used for the ROP of  $\epsilon$ -CL and  $\delta$ -VL.

### Synthesis of Cyclic Poly( $\epsilon$ -caprolactone) and Poly( $\delta$ -valeurolactone) Using (+)-1-Methyl-3-menthoxyethyl imidazol-2-ylidene

In a glove box, Schlenk flask was equipped with a magnetic stir bar, 1 g of  $\epsilon$ -CL (9.02 mmol) was dissolved in 10 mL of THF at room temperature. To this, the carbene catalyst solution was added and polymerized for 10 min. Monomer to catalyst ( $[M/C]$ ) ratios were 100 and 200, respectively. The polymerization was terminated by adding a few drops of methanol. Cyclic polymer was obtained by precipitating the polymer solution in excess methanol. The polymer product was collected by filtration followed by drying in a vacuum oven at  $50^\circ\text{C}$  for 15 h to a constant weight. The results are summarized in Table I.

Under same conditions and operations, cyclic poly( $\delta$ -valeurolactone) was prepared in 79.9% yield from 1 g  $\delta$ -VL (9.99 mmol) after polymerized for 18 min. The ratio of  $\delta$ -VL to catalyst was 125. The obtained product was analyzed by  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR, GPC, DSC, and MALDI-TOF.

### Synthesis of Cyclic Poly( $\epsilon$ -caprolactone-co- $\delta$ -valeurolactone) Using (+)-1-Methyl-3-menthoxyethyl imidazol-2-ylidene

In glove box,  $\epsilon$ -CL and  $\delta$ -VL (1 : 1 mole ratio) were added to THF at  $25^\circ\text{C}$ . To this carbene catalyst was added. The ratios of substrate to catalyst were 50, 125, and 250, respectively used. Polymerization was continued for 30 min. Polymerization was terminated by adding few drops of methanol. Crude copolymer

**Table I.** Cyclic Poly( $\epsilon$ -caprolactone) Produced by (+)-1-Methyl-3-menthoxyethyl imidazol-2-ylidene catalyst<sup>a,b</sup>

Entry no.	Cat (mmol)	[ $\epsilon$ -CL]/[Cat]	Yield <sup>c</sup> (wt %)	$T_m$ (°C)	$M_w \times 10^3$	$M_n \times 10^3$	MWD
1	0.090	100	67.6	56.48	56.1	22.4	2.5
2	0.045	200	38.6	51.54	72.6	31.9	2.27

<sup>a</sup>Solvent = THF (10 mL), Cat = precursor (+)-1-methyl-3-menthoxyethyl imidazolium chloride, carbene pretreatment conducted at 25°C for 45 min; polymerization was conducted at 25°C for 10 min with a conversion of 100%.

<sup>b</sup>GPC in THF at 25°C using polystyrene standards.

<sup>c</sup>Isolated yield.

product was obtained by precipitating the polymer solution in excess methanol in a gel form. The resulting crude product was then purified by re-dissolving in limited amounts of methylene chloride, followed precipitating with large amounts of methanol to remove residual catalyst. After filtering and drying to a constant weight in high vacuum, the copolymer product was analyzed with <sup>1</sup>H, <sup>13</sup>C NMR, DSC, and GPC spectroscopy. The results are summarized in Table II.

## RESULTS AND DISCUSSION

Catalyst precursor (+)-1-methyl-3-menthoxyethyl imidazolium chloride (**1**) was synthesized using a literature method.<sup>40</sup> The carbene catalyst derived from **1** was *in situ* generated from a reaction of **1** with potassium *t*-butoxide in THF. Previously, we demonstrated that precursor **1** based catalyst was highly efficient for the ROP of L-lactide comparing with other NHCs.<sup>40</sup> In this work, **1** showed promising activities for the ROP of  $\epsilon$ -caprolactone and  $\delta$ -valerolactone to form cyclic poly( $\epsilon$ -caprolactone) (poly( $\epsilon$ -CL)), poly( $\delta$ -valerolactone) (poly( $\delta$ -VL)) and poly( $\epsilon$ -caprolactone-*co*- $\delta$ -valerolactone) (poly( $\epsilon$ -CL-*co*- $\delta$ -VL)), respectively as summarized in Tables I and II.

The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of poly( $\epsilon$ -CL) are shown in Figure 2. All functional groups emerged in normal and expected absorptions ranges. The signals in <sup>13</sup>C-NMR spectrum [Figure 2(b)] are contributed from the carbons of **a**, **b**, **c**, **d**, **e**, and **f** in poly( $\epsilon$ -CL). No terminal groups such as -CH<sub>3</sub>O were found. MALDI-TOF MS is a powerful method for polymer characterization to determine the absolute molecular architecture, the exact mass of the repeat units and the end group masses. Figure 3 shows the MALDI-TOF MS of poly( $\epsilon$ -CL) which was obtained using dithranol as a matrix and sodium iodide as the cation source in reflector mode. In Figure 3, cyclic poly( $\epsilon$ -CL) exhibits

molecular ions having a [M+Na]<sup>+</sup> distribution. The molecular ions are separated by 114 mass units corresponding to the mass of caprolactone unit thus indicating that cyclic polymer was formed. No end groups and other population of molecular ions were detected in the MALDI-TOF mass spectrum of poly( $\epsilon$ -CL). The results suggested that the obtained polymer owns cyclic molecular architecture.

The thermal analysis of synthesized cyclic caprolactone polymer was carried out using DSC. The sample was scanned from -50°C to 80°C at a rate of 10°C/min under nitrogen atmosphere and subsequently cooled to -50°C at 10°C/min. DSC analysis was based on second heating and thermogram showed a sharp melting endothermic peak at 57°C and melting enthalpy ( $\Delta H_m$ ) of 69.8 J/g (Figure 4). The melting temperature ( $T_m$ ) is consistent with the  $T_m$  data of linear poly( $\epsilon$ -CL) isomers ( $T_m$  = 57–60°C), and thus confirms that the microstructure of poly( $\epsilon$ -CL), linear or cyclic, doesn't affect their  $T_m$ .<sup>41</sup>

ROP of  $\delta$ -VL catalyzed by precursor **1** based NHC forms the cyclic poly( $\delta$ -VL) in 79.9% yield. In MALDI-TOF mass spectrum of cyclic poly( $\delta$ -VL) (Supporting Information Figure S1), the product shows molecular ions having a [M+Na]<sup>+</sup> distribution. The molecular ions are separated by 100 mass units corresponding to the mass of VL unit thus indicating that cyclic polymer was formed. No end groups and other population of molecular ions were detected in the MALDI-TOF mass spectrum of poly( $\delta$ -VL). The results suggest that the obtained polymer owns a cyclic molecular structure. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of cyclic poly( $\delta$ -VL) (Supporting Information Figures S2 and S3) exhibit normal absorption of functional groups. Comparing with the peaks of monomer  $\delta$ -VL, the chemical shifts of all signals for cyclic poly( $\delta$ -VL) in <sup>1</sup>H-NMR spectra (Supporting Information Figure S2) were found down shifted at about

**Table II.** Cyclic Copolyesters Produced Using (+) 1-Methyl-3-menthoxyethyl imidazol-2-ylidene Catalyst for  $\epsilon$ -CL and  $\delta$ -VL Polymerization<sup>a,b</sup>

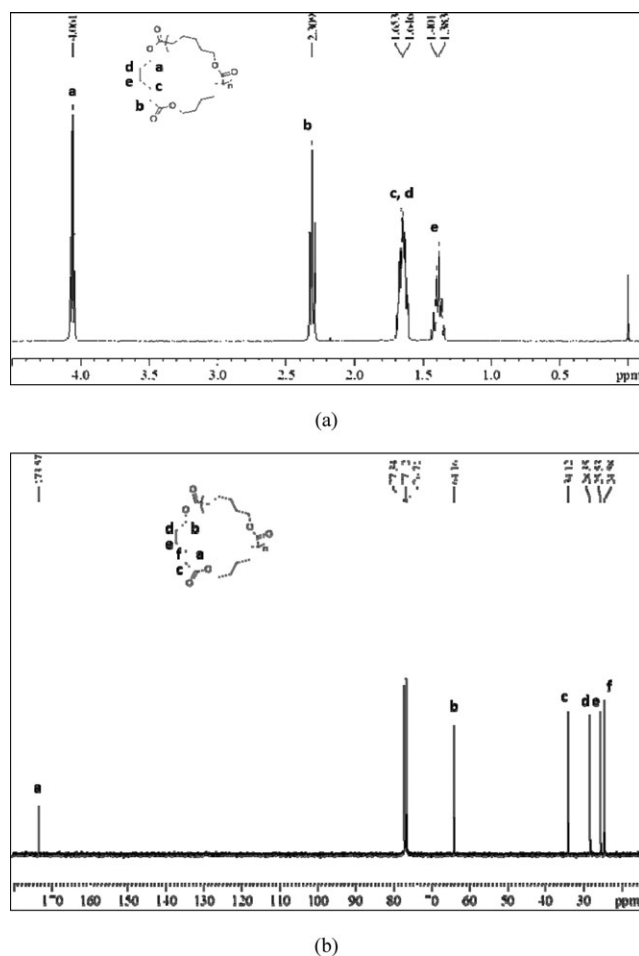
Entry no.	Cat (mmol)	CL (mmol)	VL/CL <sup>c</sup>	[CL+VL]/[Cat]	Yield <sup>d</sup> (wt %)	$T_m$ (°C)	$M_w \times 10^3$	$M_n \times 10^3$	MWD
1	0.40	9.99	1.0	50	53.2	21.4	33.3	26.1	1.27
2	0.16	9.99	1.0	125	62.6	22.0	56.6	32.9	1.71
3	0.08	9.99	1.0	250	72.1	39.8	68.2	42.9	1.58
4	0.24	19.98	0.5	125	64.9	28.0	52.7	27.6	1.91
5	0.12	4.99	2.0	125	63.2	31.0	67.3	35.4	1.9
6	0.10	2.50	4.0	125	81.7	51.5	66.1	38.5	1.71

<sup>a</sup>Solvent = THF (20 mL), Cat = precursor (+)-1-methyl-3-menthoxyethyl imidazolium chloride, carbene pretreatment conducted at 25°C for 45 min; valerolactone, 9.99 mmol; polymerization was conducted at 25°C for 30 min with a conversion of 100%.

<sup>b</sup>GPC in DCM at 25°C and calibrated using polystyrene as standards.

<sup>c</sup>Theoretical value.

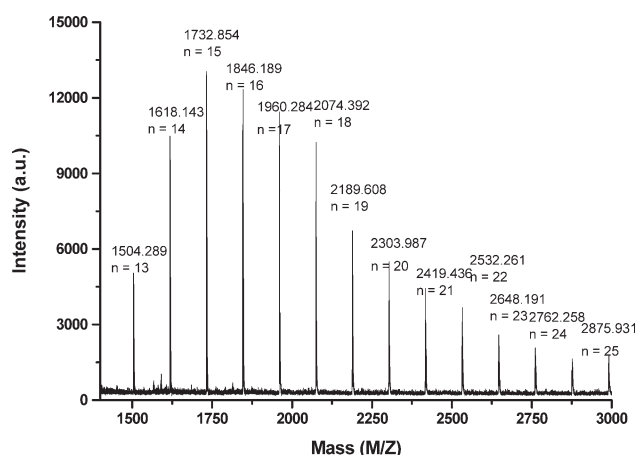
<sup>d</sup>Isolated yield.



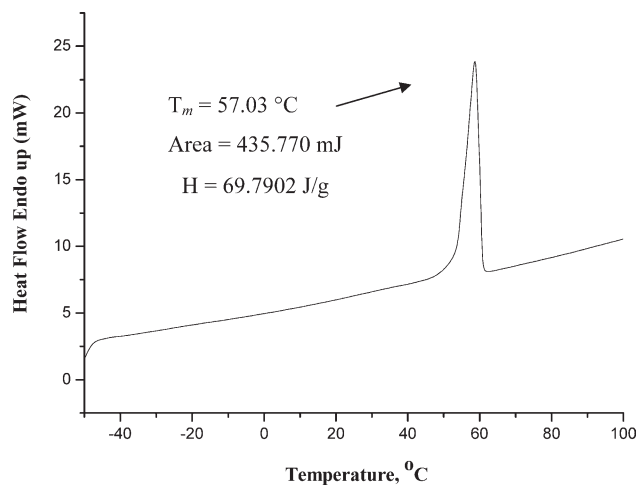
**Figure 2.**  $^1\text{H}$ -NMR (a) and  $^{13}\text{C}$ -NMR (b) spectra of cyclic poly( $\epsilon$ -CL) in  $\text{CDCl}_3$ .

0.3 ppm. This could be caused by the release of intramolecular tension from small ring to macrocycle. No terminal groups such as  $-\text{CH}_3\text{O}$  were found.

The zwitterionic ring opening copolymerization of  $\epsilon$ -CL and  $\delta$ -VL was also conducted using the NHC catalyst from precursor



**Figure 3.** MALDI-TOF mass spectrum of cyclic poly( $\epsilon$ -caprolactone).



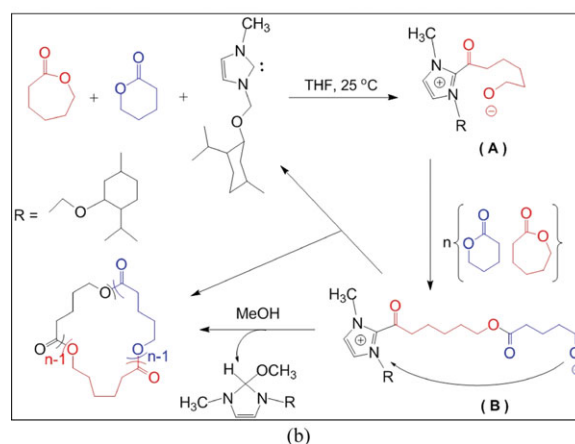
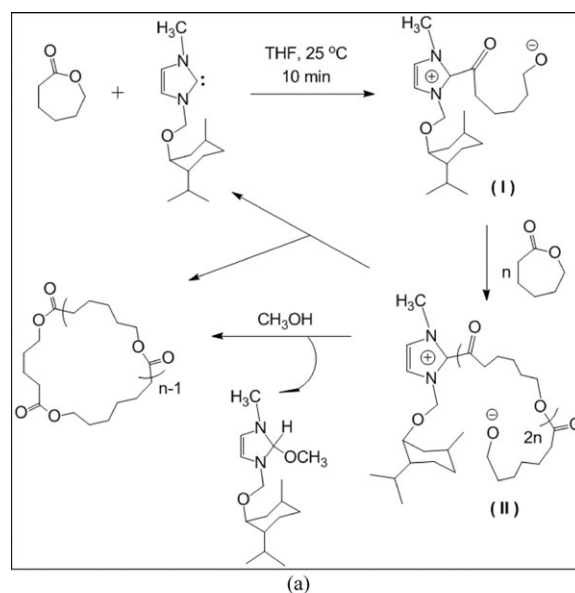
**Figure 4.** DSC thermogram of cyclic poly( $\epsilon$ -caprolactone).

I in the absence of an alcohol. The results of cyclic poly(CL-*co*-VL) copolymers were summarized in Table II. Figure 5 illustrates the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of cyclic poly(CL-*co*-VL) obtained by the polymerization of  $\epsilon$ -CL and  $\delta$ -VL in a 1 : 1 mole ratio and the ratio of [monomers]/[catalyst] equals to 125 in THF at room temperature. Proton signals of CL and VL from a to c in valerolactone and A to D in caprolactone assignable to  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ -methylene protons of the ester carbonyl moiety at  $\delta$  -2.35, 1.67, 1.4, 1.67, and 4.06 ppm. In  $^1\text{H}$ -NMR spectrum of the cyclic copolymer, only signals caused by  $\gamma$ - $\text{CH}_2$  from the carbonyl group in the  $\epsilon$ -caprolactone unit are resolved, peaks from other  $\text{CH}_2$  are overlapped, and thus it's impossible to accurately integrate the peak areas. Other functional groups show normal absorptions in  $^1\text{H}$ -NMR spectrum and well fit the expected values. No peaks of end groups in the polymer chains were detected in the  $^1\text{H}$ -NMR spectrum. Peaks in the  $^{13}\text{C}$ -NMR spectrum (Figure 5) display in normal range and are consistent with the molecular structure of the cyclic poly( $\epsilon$ -CL-*co*- $\delta$ -VL). In addition, in the  $^{13}\text{C}$ -NMR spectrum of the cyclic copolymer, fine splits were observed for the peaks contributed from methyleneoxy groups (A, a), carbonyl groups (B, b) and methylene groups (C, c) in CL and VL because of the small changes of chemical environment after polymerization. This suggests that the  $\epsilon$ -CL and  $\delta$ -VL monomers are incorporated irregularly in the cyclic copolymers.

The weight average molecular weight ( $M_w$ ) and number average molecular weight ( $M_n$ ) and molecular weight distribution (MWD) of the cyclic copolymers were determined by GPC analysis. The GPC curves of all copolymer samples show mono-model with relatively narrow MWD (Table II). The  $M_w$  and  $M_n$  of the resulting cyclic copolymers increased with the increase of the feed ratio of monomer to catalyst from 50 to 250 (Table II). At low feeding concentrations of monomer and catalyst (Table II Entry no. 5 and 6), composition of the produced cyclic copolymer was found to be disproportional and irregular. This effect was reflected on the values of  $T_m$ ,  $M_w$ , and MWD of the resulting copolymers. Although the real mechanism is not clear yet, the composition changes of the produced cyclic copolymers in the cases could be caused by a competition of random and

gradient copolymerization reactions. It should be pointed out that the cyclic copolymers by the NHC catalyst own higher  $M_w$  comparing with their linear analogues.<sup>42</sup> Even though both cyclic poly( $\epsilon$ -CL) ( $T_m = 51\text{--}57^\circ\text{C}$ , Table I) and cyclic poly( $\delta$ -VL) ( $T_m = 55^\circ\text{C}$ ) shows almost identical melting points ( $T_m$ ), the  $T_m$  values of the cyclic copolymers were found to decrease dramatically (Table II). These results further confirms the formation of cyclic random poly( $\epsilon$ -CL-*co*- $\delta$ -VL). Similar to literature, we have also demonstrated that the zwitterionic ROP catalyzed by the NHC is effective to tune both physical and chemical properties of the cyclic copolymers.<sup>43–45</sup>

In mechanism, zwitterionic ROP is an ionic polymerization in which both anions and cations are attached to the same polymer chain.<sup>46,47</sup> The efficiency of ROP of lactones is very sensitive both to the steric and electronic nature of the carbene. An electronically rich substituent is desired to enhance the catalytic effect.<sup>34–37</sup> According to literature, the proposed mechanisms

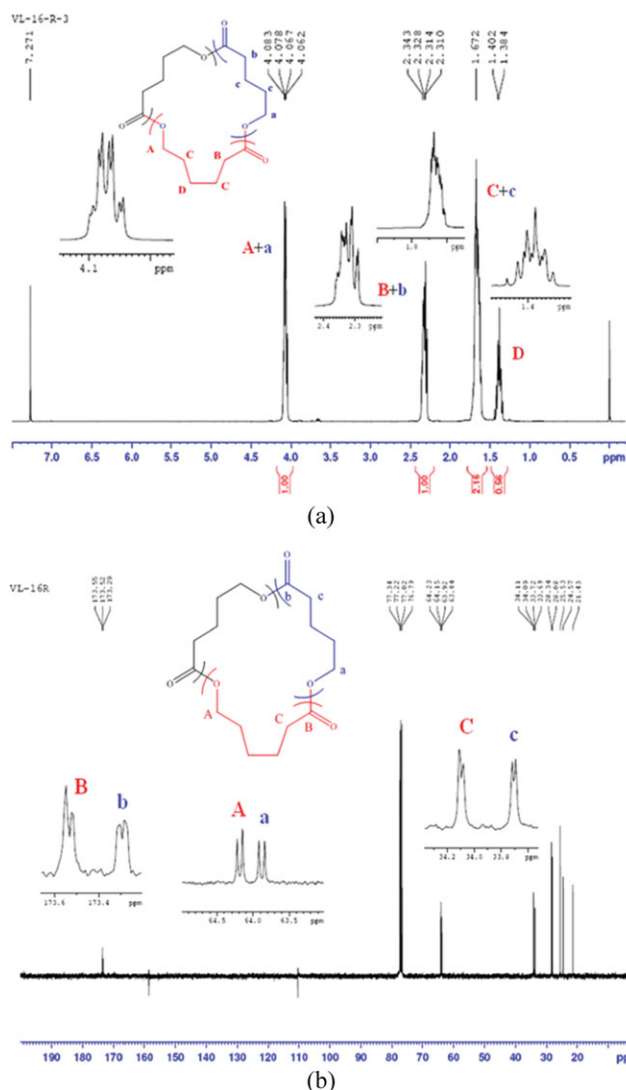


**Scheme 1.** Proposed mechanisms for the ROP to form cyclic poly( $\epsilon$ -CL) (a) and cyclic poly( $\epsilon$ -CL-*co*- $\delta$ -VL) (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

are described in Scheme 1 for ROP initiated by NHC catalyst from precursor **1** to synthesize cyclic poly( $\epsilon$ -CL), poly( $\delta$ -VL), and poly( $\epsilon$ -CL-*co*- $\delta$ -VL). In the mechanism, ROP of lactone with NHC catalyst occurs through a nucleophilic mechanism where NHC radicals initiate lactones *via* activating the carbonyl groups to form new zwitterionic species (**I** or **A**). After carrying out chain growth, zwitterionic polymer intermediates (**II** or **B**) were generated. The intermediates **II** and **B** could release polymer and NHC catalyst to realize the catalytic cycle. When methanol was added, the NHC could be deactivated by forming an O-H insertion product.<sup>48</sup>

## CONCLUSIONS

The NHC catalyst *in situ* generated from precursor (+)-1-methyl-3-menthoxyethyl imidazolium chloride was found a highly efficient catalyst for the zwitterionic ring-opening polymerization of  $\epsilon$ -caprolactone and  $\delta$ -valerolactone to form cyclic poly( $\epsilon$ -CL), poly( $\delta$ -VL), and poly( $\epsilon$ -CL-*co*- $\delta$ -VL). The resulting



**Figure 5.** (a)  $^1\text{H}$ - and (b)  $^{13}\text{C}$ -NMR spectra of cyclic poly( $\epsilon$ -CL-*co*- $\delta$ -VL). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

cyclic polymers own high  $M_w$  and relatively narrow MWD. Considering the high activity and low cost of the organocatalyst as well as the unique cyclic molecular architecture of the resulting biodegradable polymers, we are expecting extensive applications of the catalyst and material in future.

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