

Preparation and Intramolecular Cyclization of α -Carboxyl, ω -Amino Heterodifunctional Poly(ϵ -caprolactone) and Poly(δ -valerolactone) with Silica-Supported Condensation Agent

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ARTICLE INFO

Article history:

Received 20 November 2013

Received in revised form 24

January 2014

Accepted 29 January 2014

Available online 5 April 2014

Keywords:

Intramolecular amidation, cyclic PCL, cyclic PVL

ABSTRACT

Ring-opening cationic polymerizations of ϵ -caprolactone (CL) and δ -valerolactone (VL) were carried out in toluene at room temperature under argon atmosphere using *tert*-butyl 6-hydroxyhexanoate (BHH) as an initiator to obtain α -*tert*-butoxycarbonyl, ω -hydroxyl heterodifunctional poly(ϵ -caprolactone) (PCL) and poly(δ -valerolactone) PVL, respectively. The terminal hydroxy group was reacted with Boc- β -alanine to introduce BocNH group at the ω -position. Finally, deprotection reactions at both ends were carried out to obtain α -carboxyl, ω -amino heterodifunctional PCL and PVL. Intramolecular amidations of these difunctional aliphatic polyesters by using silica-supported condensation agent in high concentration successfully gave cyclic PCL and PVL.

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To Cite This Article: K. Saito, D.Ando, T. Uno, T. Itoh, Masataka Kubo., Preparation and Intramolecular Cyclization of α -Carboxyl, ω -Amino Heterodifunctional Poly(ϵ -caprolactone) and Poly(δ -valerolactone) with Silica-Supported Condensation Agent. *Aust. J. Basic & Appl. Sci.*, 8(4): 820-822, 2014

INTRODUCTION

Cyclic polymers are of current interest as a member of new macromolecular architectures. Recently, cyclic polymers have been applied to compounds having a more complex structure. Among them, supramolecules such as catenated polymers are also included. A polymer catenane is a molecular assembly that two or more cyclic polymers are joined mechanically through threading (Fig. 1).

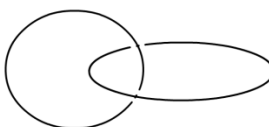


Fig. 1: Structure of polymer catenane.

Since most cyclic polymers have been prepared end-to-end ring closure of a linear precursor polymer, a straightforward synthesis of polymer catenane is to carry out an intramolecular cyclization reaction of a linear precursor polymer in the presence of another cyclic polymer which is to be threaded. Usually, the ring closure reaction is carried out under high dilution conditions to prevent side reactions including intermolecular reaction which will give linear chain-extended by-products. However, high-diluted condition is unfavorable for chain threading. That is, it is difficult to establish experimental reaction conditions which enable the intramolecular cyclization and chain threading at the same time.

If intramolecular cyclization is possible in high polymer concentration, chain threading which leads to catenated structure can occur. One possible strategy is to carry out intramolecular cyclization using solid-phase. To the best of our knowledge the only example of solid-phase cyclization of a polymer is preparation of cyclic polyester using ion-exchange resin reported by Wood *et al.*

In this work we aim at developing intramolecular cyclization of a linear polymer using solid-phase condensation agent in high polymer concentration in order to establish a fundamental synthetic strategy for catenated polymer. We will report preparation of α -carboxyl, ω -amino heterodifunctional PCL and PVL. Their intramolecular cyclization using silica-supported condensation agent will be also reported.

RESULTS AND DISCUSSION

As a representative example, Figure 2 shows synthetic pathway for α -carboxyl, ω -amino heterodifunctional PVL.

Ring-opening cationic polymerization of VL was carried out using BHH as an initiator in the presence of diphenyl phosphate according to the method² reported by Makiguchi *et al.* The terminal hydroxy group was reacted with Boc- β -alanine using water-soluble carbodiimide (WSCl) as a condensation agent to introduce NHBoc group at the chain end. Finally, acid treatment was carried out to remove the protecting groups at the both chain ends to obtain α -carboxyl, ω -amino heterodifunctional PVL. The structure of the heterodifunctional PVL was characterized by ¹H- and ¹³C-NMR, IR, and matrix-assisted laser desorption/ionisation-time of flight mass spectrometry (MALDI-TOF MS) measurements.

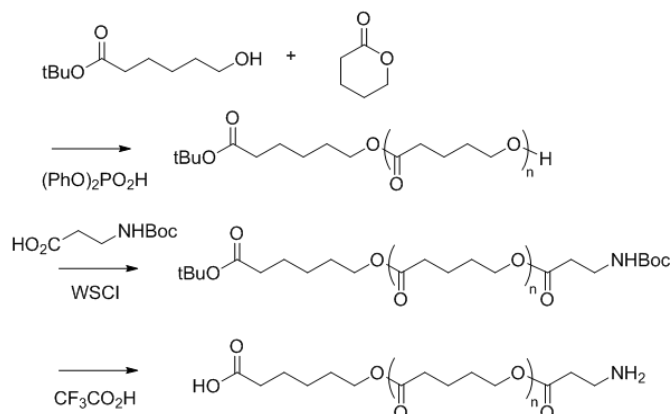


Fig. 2: Synthetic pathway for α -carboxyl, ω -amino heterodifunctional PVL.

In order to carry out intramolecular cyclization in high polymer concentration, we apply solid-phase amidation methodology using silica-supported carbodiimide condensation agent (SiliaBond[®] Carbodiimide, Si-DCC). Schematic illustration of the cyclization using Si-DCC is shown in Figure 3. The heterodifunctional polymer will react with Si-DCC to give reaction intermediate, in which α -position of the polymer is fixed to the solid. Under such circumstance, it is difficult to react intermolecularly because of the restriction of diffusion of macromolecules. As a result of suppression of condensation reaction between chains, intramolecular reaction should take place preferentially even in high polymer concentration.

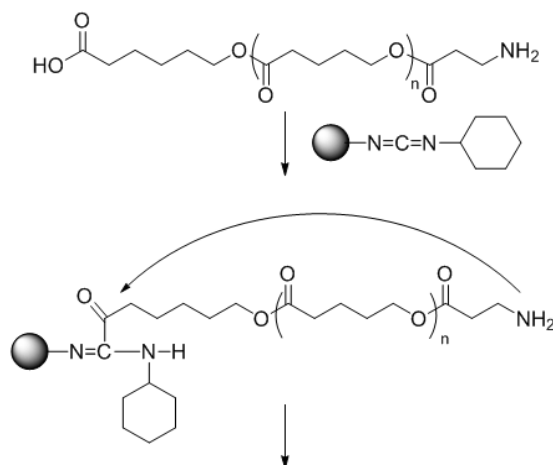


Fig. 3: Schematic illustration of intramolecular cyclization using Si-DCC.

As a control experiment, intramolecular cyclization of α -carboxyl, ω -amino heterodifunctional PVL was carried out in a conventional high dilution method ($[PVL] = 5 \times 10^{-4}$ mol/L) using 2-chloro-*N*-methylpyridinium iodide as a condensation agent according to the previously reported method³ to obtain cyclic PVL in 39% yield. The MALDI-TOF MS of the obtained cyclic PVL is shown in Figure 4. Each peak in the spectrum represents

cyclic PVL ionized with Na^+ . The observed peak masses were in good agreement with the calculated values for the proposed structure.

Then, intramolecular amidation was carried out using commercially available Si-DCC under high polymer concentration ($[\text{PVL}] = 1 \times 10^{-2} \text{ mol/L}$). The final product was purified by silica gel column chromatography. Figure 5 shows MALDI-TOF MS of the obtained products. The observed peak masses are in full agreement with the calculated masses for the cyclic PVL. Therefore, even though under high polymer concentration, intramolecular amidation took place preferentially. The yield of cyclic PVL was 32% which is close to the value obtained by high dilution method (39%).

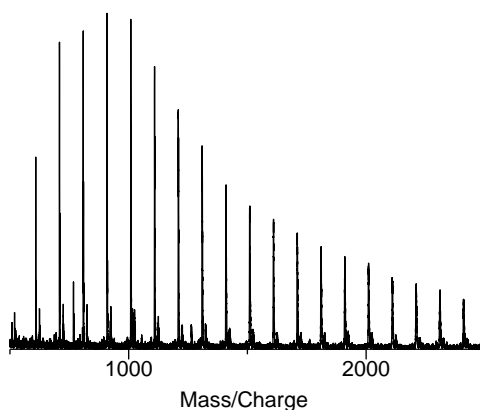


Fig. 4: MALDI-TOF MS of cyclic PVL prepared by conventional high dilution method.

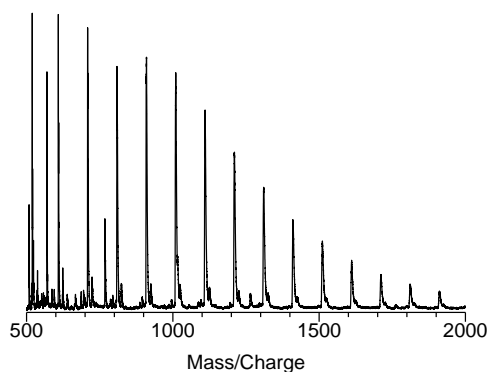


Fig. 5: MALDI-TOF MS of cyclic PVL prepared under high polymer concentration using Si-DCC.

Summary:

We prepared α -carboxyl, ω -aminoheterodifunctional PCL and PVL by ring-opening polymerizations of CL and VL, respectively. Their intramolecular cyclization reactions were carried out by using Si-DCC as a silica-supported condensation agent to give unimolecularly cyclized poly lactones in about 30% yield even under high polymer concentration. Their cyclic structure was confirmed by MALDI-TOF MS analysis. This finding is expected to open the door to the synthesis of catenated polymer.

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