# 트리메틸렌 카보네이트 단일중합체와 락티드 공중합체의 제조 및 특성

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# Preparation and Characterization of Trimethylene Carbonate Homopolymer and Copolymer with Lactide

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## 1. Introduction

Trimethylene carbonate was prepared by transesterification of 1,3-propandiol and diethyl carbonate in the presence of tin powder. Six-membered ring of TMC (trimethylene carbonate) was successfully produced from it's oligomeric state at high temperature distillation after removing the ethanol as by-product using dephlegmator. $^1$H-NMR, Mass Spectroscopy and Gas Chromatography techniques were used to confirm the purity of TMC. The yield of TMC was increased from 30% to 75% with the variation of different experimental conditions.

It has been known that random copolymerization is an useful method to prepare new materials, whose properties are different from those of the parent homopolymers and sometimes the average of them. Poly(trimethylene carbonate) (PTMC) is an amorphous polymer and has the rubber elastic behavior. So, the properties of brittle aliphatic ester linkage of poly(L-Lactide) can be modified by the copolymerization of TMC with L-Lactide. Furthermore the carbonate linkage in the polymer chain may be expected to be hydrolyzable and more hydrolytically stable than an ester linkage. Present work aims the synthesis and characterization of the TMC homopolymer and it's copolymer with L-lactide in the presence of stannous octoate catalyst using bulk polymerization method.

## 2. Experimental

### 2.1 Materials

L-Lactide was purified by recrystallization from dry ethyl acetate and dried in

a vacuum oven at room temperature for 2 days. The catalyst stannous octoate and all other chemicals were purchased from Aldrich and were purified by the standard methods.

### 2.2 Synthesis of monomer

1,3-propanediol (1.0 *mol*), dimethyl carbonate (1.5 *mol*) and catalyst (0.02 *mol*) were added to a 0.25 liter three-necked flask, fitted with a mechanical stirrer. Under the protection of nitrogen, distillation was carried out using a condenser (water cooler) for 6 hours at oil bath temperature of 150℃. The ethanol by -product was removed using water circulator at 80℃. After completing the distillation, the oil bath temperature was lowered to 130℃ and condenser was taken out. The distillation was further continued under slight vacuum to remove by-product and unreacted residue which was purified under a high vacuum (bath temperature up to 180 ℃). The main-fraction of the product was taken out from the flask and applied for recrystallization in acetone/diethyl ether. After being dried in a vacuum for 24 hours, it was packed under the vacuum and kept in freezer. Trimethylene carbonate is colorless needle shaped solid, having melting point 45.5 ~46.5℃, Yield : 75%, $^1$H NMR ($CDCl_3$, TMS, *ppm*): 4.47 (t, 4H), 2.16 (quint., 2H).

### 2.3 Homopolymerization of TMC

2.4994 *g* (0.0245 *mol*) of TMC was charged into a flame-dried glass tube. The system was connected with a vacuum line, then dried at 110℃ for 30 minutes and purged with nitrogen. Under nitrogen 0.316 *ml* ($1.23\times10^{-5}$ *mol*) of $Sn(Oct)_2$ solution was charged into the tube with a flame-dried syringe. After sealed under reduced pressure, it was heated and kept at 120℃ for 10 hours. The homopolymer was purified twice by the dissolution/precipitation method with methylene chloride as the solvent and ether as the nonsolvent, then dried in vacuum at ambient temperature to constant weight. $^1$H NMR ($CDCl_3$, TMS, *ppm*): 4.24 (t, 4H), 2.06 (quint., 2H).

### 2.4 Copolymerization of TMC with L-Lactide

The molten ring-open polymerization was carried out in a flame-dried glass tube. The system was connected with a vacuum line, then dried at 110℃ for 30 minutes and purged with nitrogen. Under nitrogen different concentration of $Sn(Oct)_2$ solution was charged into the tube with a flame-dried syringe. After sealed under reduced pressure, it was heated and kept at 140℃ for 36 hours. The copolymer was purified twice by the dissolution/precipitation method with chloroform as the solvent and ethanol as the nonsolvent, then dried in vacuum at ambient temperature to constant weight.

## 3. Results and discussion

The ring-openning copolymerization of L-Lactide and trimethylene carbonate was carried out in the molten state at 140℃ for 36 hours. *Figure 1* showed the increasing order of inherent viscosity with the decreasing of catalyst concentration.

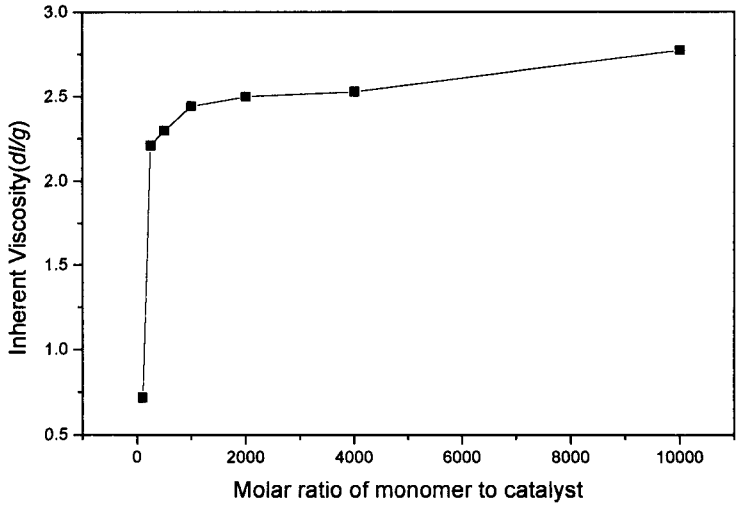
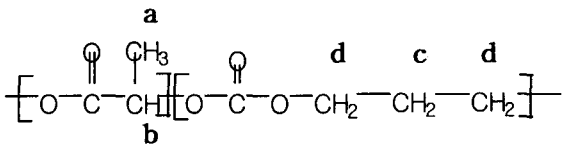



Figure 1. Effect of catalyst concentration on dilute solution viscosity of the copolymers.

*Figure 2* presented the $^1$H-NMR spectrum of a copolymer containing about 80 *mol* % TMC. The chemical shift of **d** was assigned to the four protons -O-$CH_2$- of the TMC units, and the chemical shift of **c** belonged to the two protons -OCH$CH_2CH_2$OCO- of the TMC. Where as the chemical shifts of **a** and **b** belonged to the -CH3 and -CH- of the lactide proton, respectively. The copolymer composition was calculated using the $^1$H-NMR spectrum.

*Figure 3* showed the FTIR spectra of PTMC. The peaks at 1751 and 1244 $cm^{-1}$to the C=O stretching and the -O-C-O- asymmetric stretching frequencies of PTMC, respectively.

From the DSC, only the Tg was observed, but no any endotherms for melting point which represented the semicrystalline nature of TMC homopolymer and it's copolymer with LLA.



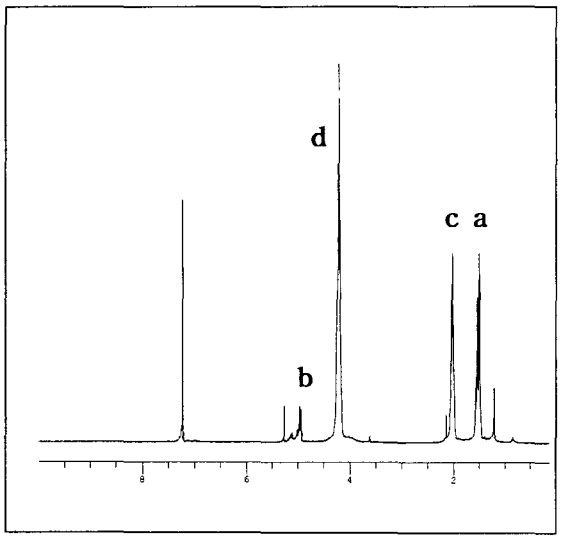




Figure 2. $^{1}$H-NMR spectrum of poly (LLA-co-80 mol % TMC).

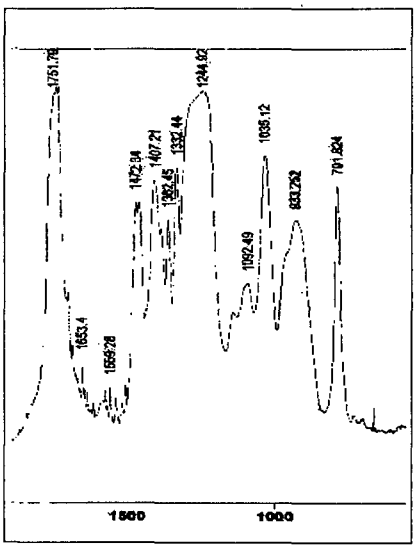



Figure 3. FTIR spectra of PTMC.

## 4. References

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