# Trimethylene Carbonate 와 ε-caprolactone ABA 트리블럭 공중합체의 합성 및 특성

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# Synthesis and Characterization of ABA Type Block Copolymers of Trimethylene Carbonate and ε-caprolactone

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## 1. Introduction

A series of ABA type triblock copolymers of trimethylene carbonate (TMC) and ε-caprolactone(ε -CL) with different molar ratio were synthesized using ethylene glycol as initiator and stannous octoate as catalyst by ring-opening bulk polymerization. The characterization of the triblock copolymers was characterized by $^{1}$H-NMR, $^{13}$C-NMR, FT-IR, GPC and DSC, and compared with random copolymer. The mechanical properties of the copolymers were studied using tensile tester. The thermal and mechanical properties of copolymers with different compositions were investigated.

## 2. Experimental

### 2.1 Materials

ε-CL was distilled over $CaH_2$ prior to use. TMC was synthesized according to the literature and purified by re-crystallization using acetone and diethyl ether as solvent, and dried under vacuum before using. Ethylene glycol was distilled under reduced pressure. Stannous octoate was used as received.

### 2.2 Pre-polymerization and copolymerization

ε-CL, stannous octoate(catalyst) and ethylene glycol(initiator) put into flame-dried glass tubes. The molar ratio between catalyst and ε-CL was 1: 10000 and that of initiator and ε-CL was 1:100. Then, the flame-dried glass tubes were sealed under reduced pressure. They were immersed in an oil bath at 130℃ for 30h. The obtained product was dissolved in methylene chloride and then precipitated in cold diethyl ether. Finally, this was extracted in ethanol and dried under vacuum. The copolymerization process was similar to the pre-polymerization.

## 2.3 Measurement

The copolymers were characterized by $^{1}H$ NMR, $^{13}C$ NMR, FT-IR, GPC and DSC. The mechanical properties of the copolymers were checked using tensile tester.

## 3. Results and discussion

$^{1}H$ NMR spectra of pre-polymer proved that the ethylene glycol has successfully initiated the polymerization of ε-CL. Then various molar ratios of TMC monomer to the pre-polymer have been used to synthesize different ABA type block copolymers. The reaction was carried at 120℃ and for 88h. $^{1}H$ NMR spectra of the block copolymer indicated that the pre-polymer successfully initiated the polymerization of TMC monomer. GPC curves also confirmed the successful synthesis of the block copolymers. $^{13}C$ NMR spectra of copolymer of the block copolymer showed that the resulting copolymer was a block copolymer and not a random copolymer. Thermal properties of the block copolymer and the random copolymer of TMC and ε-CL were investigated by DSC. For the random copolymer, there was only single glass transition temperature, Tg and one melting temperature, Tm. For a series of the block copolymers, two Tg and one Tm were found. The mechanical properties of ABA type block copolymers of TMC and ε-CL were investigated. The obtained results are listed in Table 1. Because the film sample of Nb1 was very brittle, and Nb5 very sticky, they could not be checked on the instrument. It was observed that block copolymers with different molar ratio possessed different mechanical properties. Sample Nb3 with molar ratio 50/50 (TMC/ε-CL) showed the highest tensile stress at maximum and elastic modulus. Its stress-strain curve belonged to stiff and tenacity type. Stress-strain behavior of Nb2 was found weak and brittle and that of Nb4 weak and soft.

Table 1. Mechanical properties of block copolymers [a]

| Sample | TMC/ε-CL (mol/mol) | Tensile stress at maximum ( MPa ) | Tensile strain at maximum ( % ) | Elastic moduli ( MPa ) |
|---|---|---|---|---|
| Nb1 | 10/90 | - | - | - |
| Nb2 | 30/70 | 101 | 2 | 46 |
| Nb3 | 50/50 | 2.1 | 11 | 172 |
| Nb4 | 70/30 | 0.2 | 44 | 11 |
| Nb5 | 90/10 | - | - | - |

[a] Average values of several block copolymers

## 4. CONCLUSION

ABA type triblock copolymers of trimethylene carbonate and ε-caprolactone were successfully synthesized using ethylene glycol as initiator, stannous octoate as catalyst. The thermal properties as well as mechanical properties of the copolymers changed considerably with copolymers of different composition. Block copolymers of different thermal behaviors and different mechanical properties can be obtained by adjusting the composition of the copolymers.

## 5.References

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