

Trimethylene Carbonate와 ϵ -caprolactone를 이용한 ABA 형태 공중합체 합성에 관한 연구

가영당, 김학용, 이덕래, 정빈*, 나라얀 바타라이*
전북대학교 섬유공학과, *전북대학교 유기신물질공학과

Synthesis of ABA-type Block Copolymer of Trimethylene Carbonate and ϵ -caprolactone

Yong Tang Jia, Hak Yong Kim, Douk Rae Lee,
Ding Bin*, Narayan Bhattarai*

Department of Textile Engineering, Chonbuk National University, Chon-ju, Korea
**Department of Advance Organic Material Engineering, Chonbuk National University,
Chon-ju, Korea*

1. Introduction

Over the last 20 years, biodegradable materials in medical applications have been studied extensively. Among these materials, poly(ϵ -caprolactone) and poly(trimethylene carbonate)(PTMC) are attractive biopolymers to be used as biodegradable sutures, artificial skin, drug release system. It was known that PCL is a nontoxic biocompatible semicrystalline polymer with melting point of 63°C, and PTMC is an amorphous or little crystalline polymer. The hydrolytic degradation rate of PTMC is slower in in-vitro. But more rapid in-vivo than that of PCL. The properties of the copolymers of caprolactone and trimethylene carbonate are different from their homopolymers. The copolymers of PCL and TMC have been studied with great interest. In this article, ABA-type block copolymers of PCL pre-polymers and trimethylene carbonate with stannous octanoate as the catalyst at certain temperature for sometime by the bulk polymerization has been investigated.

2. Experimental

2.1 Materials

ϵ -CL was dried and distilled over CaH₂ under reduced pressure. Trimethylene carbonate was prepared by exchange reaction of 1,3-propanediol and diethyl carbonate. It was further purified by recrystallization and dried just before use. Ethylene glycol was purified by distillation under reduced pressure. Stannous

octannoate, methylene chloride, ether, ethanol were used as received.

2.2 Synthesis of pre-polymers and block copolymers

ϵ -CL stannous octanoate (according to certain ratio of molar) and ethylene glycol as initiator were weighed into flame-dried glass tube. Then the glass tube was sealed under reduced pressure and heated. The glass tube was then immersed in oil bath at certain temperature for certain time. After the reaction was completed the product was dissolved in methylene chloride and then precipitated with cold ether and extracted in ethanol and then dried under vacuum. Block copolymers were synthesized by similar process using PCL prepolymer and trimethylene carbonate as reaction materials.

2.3 Characterization

The obtained polymers were characterized by ^1H NMR spectroscopy and ^{13}C NMR spectroscopy using CDCl_3 as the solvent. Inherent viscosity was also checked.

3. Results and Discussion

ABA-type block copolymers were prepared through two step reactions. First, PCL pre-polymers were synthesized by using ethyl glycol as initiator and stannous octanoate as catalyst. Second, the block copolymers were obtained by using trimethylene carbonate as monomer and stannous octanoate as catalyst. Thus obtained PCL pre-polymers possessed hydroxyl end groups. Boettcher has reported that in the stannous octanoate catalyzed polymerization of D,L-lactide, no transesterification reactions occurred at reaction temperatures below 120°C . According to this point of view, it was believed that the hydroxyl groups of the PCL pre-polymers initiated the polymerization of trimethylene carbonate. The reaction temperature for synthesis of PCL pre-polymers was 140°C and the reaction time was 30h. The reaction temperature for the second step was 120°C . *Figure 1* shows time dependence of inherent viscosity($[\eta]$) of the copolymers with ϵ -CL/TMC feed ratio of 50/50(mol/mol). It was found that the $[\eta]$ of copolymers increase with increase of time until after $[\eta]$ of the copolymers came to a constant. Therefore, the synthesis of the copolymers was carried out at 120°C for 144h. *Figure 2* has shown that ^1H NMR signals of HOCH_2 -(3.69ppm) hydroxyl end group of the PCL and the signal of the protons of $-\text{OCH}_2\text{CH}_2\text{O}$ -(4.06ppm) bond with the caproyl units were detected. This proved that the ethylene glycol has successfully initiated the polymerization of ϵ -CL. *Figure 3* has shown that ^1H NMR signals of block copolymers of PCL and TMC. The signals of HOCH_2 -methylene protons of the hydroxyl end groups of PCL pre-polymers at 3.69 ppm were found disappeared. These results proved the successful initiation of trimethylene carbonate. In the ^{13}C NMR spectra(*Figure 4A*) of the block copolymers and random polymer (CO region only) of ϵ -CL(C) and TMC(T), not only signals of TTT and CCC sequences but also other sequences were found.

But in the ^{13}C -NMR (*Figure 4B*) spectra of the block copolymers of ϵ -CL and TMC no signals belonging to other sequences were found.

4. Conclusion

PCL pre-polymers with hydroxyl end groups were prepared by using ethylene glycol as initiator and $\text{Sn}(\text{Oct})_2$ as catalyst. ABA-type block copolymers of trimethylene carbonate and ϵ -caprolactone could be synthesized using PCL pre-polymers and monomer of trimethylene carbonate.

5. References

- 1) Kricheldorf HR, Boettcher C, Tønnes K-U. *Polymer*, **33**, 2817(1992).
- 2) C. A. P. Joziase, Hans Grablowitz, A. J. Pennings, *Macromol. Chem. Phys.*, **201**,107-112(2000).
- 3) Grijpma DW, Zondervan GJ, Pennings AJ, *Polym. Bull*, **25m**, 1281(1991).
- 4) Hiljiane Vainio M, Karjalaine T, Seppala J, *J Appl. Polym. Sci.*, **59**, 1281 (1996).
- 5) J. C. Middleton, A. J. Tipton. *Biomaterials*, **21**, 2335-2346(2000).
- 6) J. G. Ryu, Y. I. Jeong. *International Journal of Pharmaceutics*, **200**, 231-242(2000).

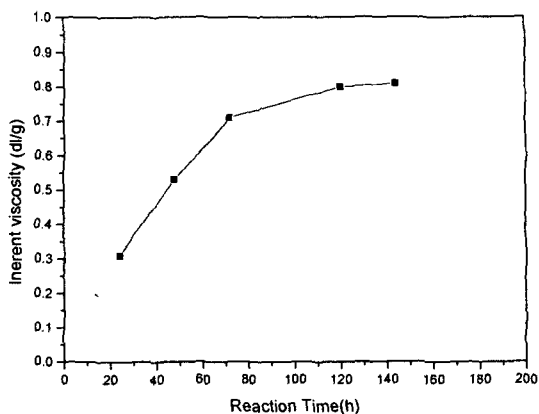


Figure 1. Inherent viscosity ($[\eta]$) of ABA-type block copolymer as a function of reaction time

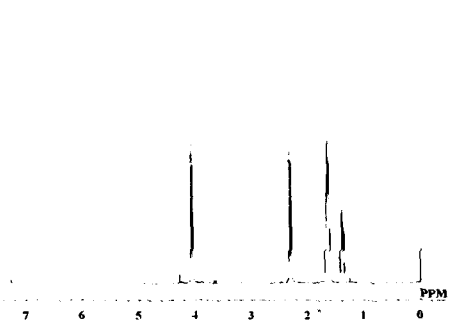


Figure 2. ^1H NMR spectra of Pre-polymer of ϵ -caprolactone

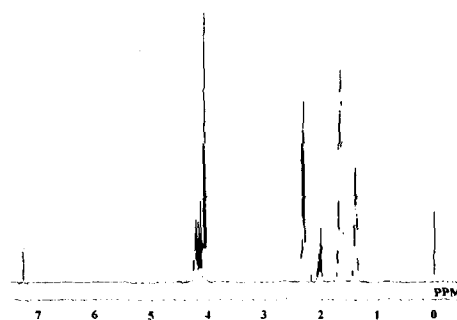
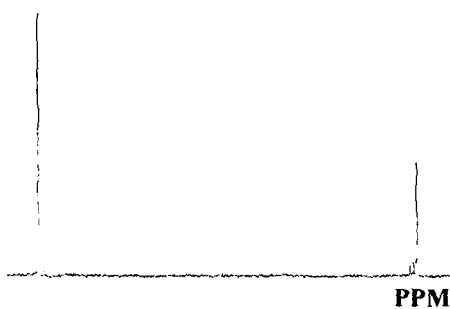


Figure 3. ^1H NMR of block copolymer of trimethylene carbonate and ϵ -caprolactone

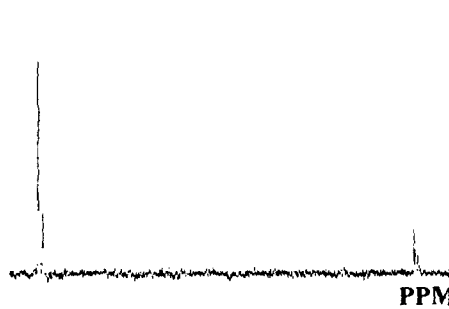


172.5

PPM

155

(A)



172.5

PPM

155

(B)

Figure 4. ^{13}C -NMR of spectra of CO region only (A :Block copolymer B :Random copolymer)