

사카라이드로부터 제조한 새로운 생분해성 폴리에스테르

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Novel Biodegradable Polyester Based on Saccharides

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1. Introduction

Recently, synthetic polymers containing units of carbohydrate derivatives with pendant functional groups have been much studied. The polymers should be able to be used drug carriers and scaffold for tissue engineering because of their nontoxicity, biocompatibility, and biodegradability.¹⁻⁶ During the last three decades, various polyfunctional polymers, e.g. polyhydroxypolyamides and polyesteramides, based on carbohydrates have been reported and synthesized by condensation polymerization between sugar derivatives and diamines, although it could be done via complicated reaction routes going through protecting.¹⁻⁶ Those polymers have had problems of complicated reactions, flexibility, and so on.

In this study, we tried to synthesize for the first time the polyhydroxypolyesters by reacting a monosaccharide, galactaric acid, with ethylene glycol. To avoid complicated protecting-deprotecting steps in the synthesis, we tried direct polycondensation of one or two stages. Polymerization behavior was monitored as functions of conversion, molecular weight change, catalytic effects, etc,

2. Experimental

2.1. Materials

Galactaric acid(mucic acid) was purchased from Aldrich Chemical Co.. Ethylene Glycol was purchased from Junsei Chemical Co.. Antimony trioxide was obtained from Fluka Chemicals. Sodium acetate was purchased from Kanto Chemical Co.. All chemicals were used without further purification.

2.2. Synthesis

Esterification of bishydroxyethyl galactarate (BHEG)

Various mole ratios of galactaric acid to ethylene glycol and various kinds of catalysts were added into a nitrogen-purged 250ml three-neck round bottom flask equipped with Dean-Stark trap, and the reaction mixture was stirred at 120°C for 24h.

Polycondensation of poly(ethylene galactarate) (PEGA)

BHEG was put into a 250ml three-neck round bottom flask equipped with a reflux condenser that was connected with a vacuum system through a cold trap, and was stirred under vacuum at 120°C for 6h to produce PEGA through polycondensation reaction. After reaction, the polymers (PEGA) were dissolved in methanol, and subsequently were precipitated into chloroform to remove residual solvent. Finally, the polymers were dried in a vacuum at 80°C for 24h.

2.3. Characterization

FTIR spectra were obtained on a PerkinElmer, spectrum GX FTIR spectrometer. $^1\text{H-NMR}$ spectra were obtained from a Bruker, Avance 500 operating at 500MHz for proton.

3. Results and Discussion

Synthesis of bishydroxyethyl galactarate (BHEG)

The prepolymer, BHEG was synthesized by esterification reaction of galactaric acid and ethylene glycol with several catalysts. Figure 1 shows that antimony trioxide was most effective.

Synthesis of poly(ethylene galactarate) (PEGA)

The polyester, PEGA was prepared by transesterification reaction between BHEGs. It was found that there were two kinds of PEGAs. One was the polymer that could be dissolved in common polar organic solvents, especially water. That should be able to be used biomedical applications. Another was micro-fibers that was not soluble in common organic solvents, and which consist of nano-fibrils. The structure of the polymer was analyzed by FTIR(Fig. 2), $^1\text{H-NMR}$.

4. Conclusions

Novel biodegradable polyesters having pendant hydroxyl groups were synthesized by polycondensation reaction of galactaric acid and ethylene glycol with catalysts. Two kinds of polymers were synthesized, water soluble polyester and non-soluble fibers.

5. References

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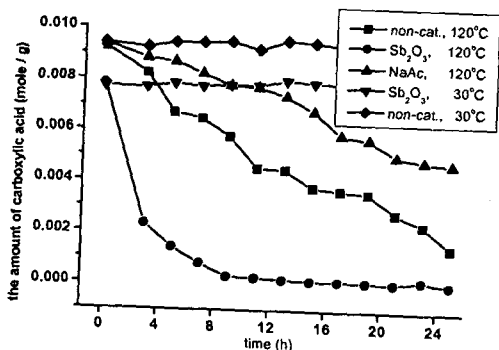


Figure 1. End group analysis during BHEG synthesis

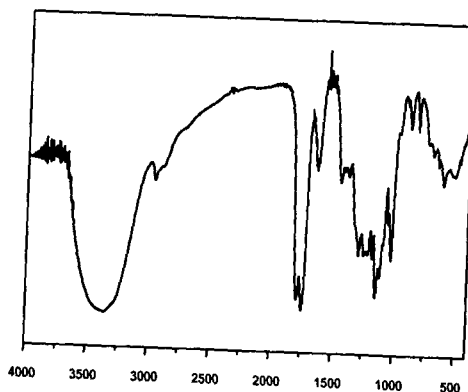


Figure 2. IR spectrum of PEGA