Facile Synthesis of Novel Hyperbranched Polyester from A2 and B3
Hongliang Cao, Wenxin Wang*, Abhay Pandit*
Network of Excellence for Functional Biomaterials, National University of Ireland, Galway
Wenxin.wang@nuigalway.ie, Abhay.pandit@nuigalway.ie

Introduction
There are large number of applications in drug delivery and tissue engineering for ester-type polymers, such as PLGA\(^1\). In the past two decades, hyperbranched polymers, including hyperbranched polyester, have received increasing attention due to their unique architectures and intrinsic properties, such as, large amounts of branch points and end groups, excellent solubility and low viscosity in solvents\(^2\). Hyperbranched polyesters have been synthesized mainly by ABx (x>1) type monomers\(^3\). Here we report a facile one-pot polymerization method toward a novel hyperbranched polyester, which was made from commercially available aconitic acid (B3) and diethylene glycol (A2). Although ideal A2 + B3 method tends towards gelation, we can synthesize hyperbranched polyester by producing in-situ an ABx-type monomer by an A2 + B3 method.

Materials and Methods
To a complete dry two-necked flask, 0.02mol aconitic acid and 0.03mol diethylene glycol were dissolved into 30 ml anhydrous tetrahydrofuran (THF). The flask was equipped with a soxhlet extractor and a condenser. In soxhlet extractor, 20g anhydrous 4 Å molecular sieves were pre-charged. After purging by argon gas, the reaction system was heated and THF was permitted to reflux through molecular sieves and redirected back to the flask to remove water. After that, the product was purified and characterized by GPC and NMR.

Results and Discussion
The molar ratio of starting materials, aconitic acid (B3) and diethylene glycol (A2), was set at 2:3, which means the ratio of carboxylic acid group and hydroxyl group is 1:1. A brown viscous polyester sample was obtained. GPC results showed that the Mn of as-prepared sample is about 216 KDa, and polydispersity (PD) of the polyester is 4.3, which indicates that we can synthesize polyesters with high molecular weight via a facile one-pot method.

The structure of polyester was further characterized by \(^1\)HNMR (figure). The characteristic peak of vinyl proton was located at 7.2 ppm. Composition of the polyester was calculated from the integral data. The molar ratio of diethylene glycol and aconitic acid was calculated as 9:4 for the polyester, which was in accordance with the theoretical value obtained by complete diethylene glycol end-capping ( (2n+1) : n , where n represents the molar amount of aconitic acid ).

Fig. \(^1\)HNMR spectra of A2 + B3 hyper branched polyester at molar ratio of 3:2.

Conclusion
The novel hyperbranched polyester with high molecular weight was successfully made from A2 + B3 via a facile one-pot method. This hyperbranched polyester is alcohol end-capped at the starting A2 and B3 ratio of 3:2. Further study of the polyester for tissue engineering is ongoing.

References

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