Zwitterionic Polymerization with $B(C_6F_5)_3$: a Simple Access to Branched Cyclic Polyglycidol

F. Barroso-Bujans[1,2,3]

[1]*Donostia International Physics Center (DIPC), Paseo Manuel Lardizábal 4, 20018 San Sebastián (Spain)*
[2]*Centro de Física de Materiales, CSIC-UPV/EHU, Paseo Manuel Lardizábal 5, 20018 San Sebastián (Spain)*
[3]*IKERBASQUE - Basque Foundation for Science, María Díaz de Haro 3, E-48013 Bilbao (Spain)*
Email: fbarroso@dipc.org

Introduction

Cyclic polymers possess unique physico-chemical properties compared to their linear counterparts as a result of the absence of end-groups and their more compact conformation. The overall interest over these cyclic structures or rings is really growing. Today, there are two primary methods for the synthesis of cyclic polymers: (1) ring closure and (2) ring expansion polymerization. In particular, the electrophilic zwitterionic ring expansion polymerization (eZREP) of epoxides with $B(C_6F_5)_3$ was proposed in our group already in 2014 for the synthesis of cyclic polyethers [1] and copolyethers [2] containing a diversity of functional side groups.

Polyglycidol (PG) is a polyether used in biomedical and pharmaceutical applications. The hydroxyl groups of PG render it with multiple choices for chemical modification and immobilization of drugs. The linear and hyperbranched forms of PG have been very much studied. However, very few is known about the cyclic structure of PG.

In present study we expand upon our previous reports and present a complete study on the synthesis of cyclic polyglycidol (cPG) in bulk and quasi-bulk conditions by using $B(C_6F_5)_3$ as a catalyst and glycidol as a monomer. We include kinetic experiments that evidences an abrupt chain growth at high monomer conversions. Ring fusion and branching mechanisms are invoked to explain such phenomenology. Branched cPG are the major compounds with M_n up to 8 kg/mol and $Đ \sim 2$. In the presence of large amounts of water ($[H_2O]/[B(C_6F_5)_3] >>1$), $B(C_6F_5)_3$ is still active producing branched linear polyglycidols with M_n ~1.2 kg/mol. The non-dependence of the glass transition temperature on topology and branching indicates that these architectural features play a secondary role behind a most important factor that is the formation of associated networks induced by hydrogen bonds. This study has been recently submitted for publication [3].

Experimental

Bulk and quasi-bulk polymerization of glycidol was carried out in roundbottom flasks under magnetic stirring. 0.5 mL of glycidol was cooled to 0 ºC and then, corresponding amounts of $B(C_6F_5)_3$ were added. $[Gly]_0/[B(C_6F_5)_3]_0$ mol ratios of 297, 594 and 799 were used. In quasi-bulk conditions, $B(C_6F_5)_3$ was previously dissolved in 86 μL of a solvent. Termination was done by addition of methanol after 2, 24 or 48h. The obtained PG was precipitated in diethyl ether and dried at 60 ºC in a vacuum oven overnight.

Results and Discussion

The polymerization of glycidol in solvents such as dichloromethane, chloroform and toluene has the disadvantage of exhibiting a change in solubility from monomer to polymer causing the precipitation of the polymer over the course of the polymerization. PG is soluble in polar solvents such as water, methanol, pyridine and N, N-dimethylformamide. None of them can be used in the eZREP of glycidol due to an inhibition of the catalytic activity of $B(C_6F_5)_3$. Therefore, the solvent

choice is very limited. In this study, bulk or quasi-bulk polymerizations were able to generate branched cPG in very high yields (~99 %). Our results demonstrate that molecular weight can be tuned by varying the reaction conditions such as the temperature, the monomer to catalyst ratio, and by adding molecular sieves in bulk conditions.

Kinetic experiments demonstrated that the molecular weight of the polymer is triggered at high conversions which can be explained by the occurrence of transfer reactions such as branching and ring fusion (Figure 1).

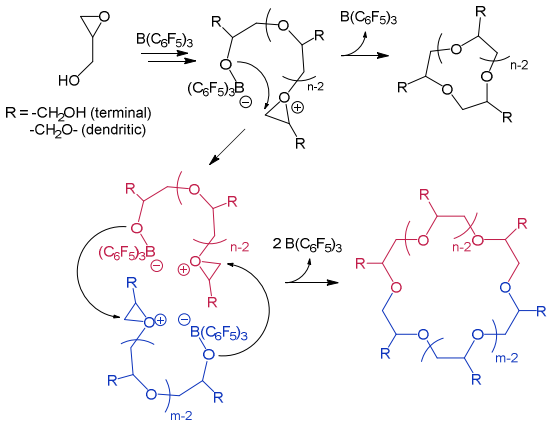

Figure 1. Mechanisms of ring formation by intramolecular and intermolecular (ring fusion) reactions.

By using low amounts of solvents of different polarities in quasi-bulk conditions (17 vol%) precipitation of the polymer is avoided and the molecular weight tuned. With decreasing solvent polarity, the molecular weight increases approaching that obtained in bulk conditions, whereas by increasing the solvent polarity the molecular weight decreases.

By adding water to the polymerization reaction, shorter chains are formed, as expected, and an increasing number of branched linear polyglycidol chains are generated compared to the cyclic ones. A competition for the epoxide oxygen between $B(C_6F_5)_3$ and H^+ during initiation would explain the growth of both cyclic and linear specimens in the presence of water. Interestingly, the polymerization goes to high monomer conversions even by adding large amount of water ($[H_2O]$ / $[B(C_6F_5)_3]$ >> 1) evidencing the high reactivity of the catalyst towards the glycidol monomer.

Investigations of the glass transition temperature of branched cPG, branched linear PG and unbranched linear PG showed a clear non-dependence with the polymer architecture (Figure 2). The difference in T_g with literature data can be explained by the different amount of water in the samples as a result of different preheating treatments. The formation of associative networks introduced by the large number of hydroxyl groups in the structure would predominate over the chain architecture, leaving a secondary role to topology and branching.

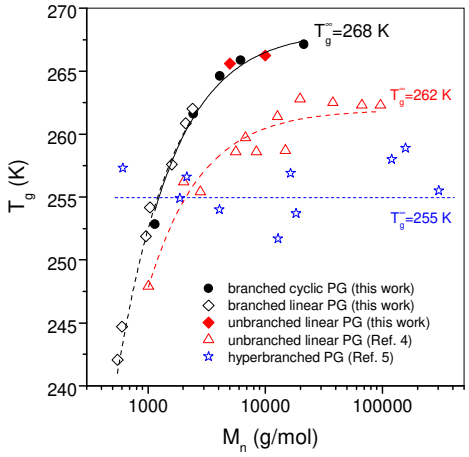

Figure 2. DSC Tg of PG obtained in this study and from the literature [4, 5].

Acknowledgements

MICINN/FEDER, UE, PGC2018-094548-B-I00; Basque Government: IT-1175-19, PIBA 2021-1-34 and Prov. Council of Gipuzkoa: RED 2021:ID44.

References

1. Asenjo-Sanz, I., Veloso, A., Miranda, J.I., Pomposo, J.A., Barroso-Bujans, F. (2014). Polym. Chem. 5, 6905-6908.
2. Asenjo-Sanz, I., Veloso, A., Miranda, J.I., Alegría, A., Pomposo, J.A., Barroso-Bujans, F. (2015). Macromolecules 48, 1664-1672.
3. Al Assiri, M.A., Gómez Urreizti, E., Pagnacco, C.A., Gónzalez de San Román, E., Barroso-Bujans, F. (Submitted).
4. Osterwinter, C., Schubert, C., Tonhauser, C., Wilms, D., Frey, H., Friedrich, C. (2015). Macromolecules 48, 119-130.
5. Schubert, C., Osterwinter, C., Tonhauser, C., Schömer, M., Wilms, D., Frey, H., Friedrich, C. (2016). Macromolecules 49, 8722-8737.