Dynamics of cyclic polyethers by broadband dielectric spectroscopy

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Cyclic polymers possess unique physico-chemical properties compared to their linear counterparts as a result of the absence of end-groups and the equivalence of all monomer units. These differences may be expressed in their hydrodynamic, rheological, optical and thermal properties.

We will discuss our recent efforts to synthesize cyclic polyethers decorated with side chains (Figure 1)^{1,2} and to characterize them by the use of broadband dielectric spectroscopy (BDS). In particular, we will show what BDS can tell us about the local, segmental and chain dynamics of cyclic poly(glycidyl phenyl ether) compared to those of its linear analog. First of all, our cyclic and linear poly(glycidyl phenyl ether) are amorphous samples, an important characteristic that allows dielectric characterization at a broad range of temperatures. Secondly, the suppresion of the end-to-end relaxation in cyclic polymers is not trivial, as it can appear in cyclic chains with non-regio regular structures. Thirdly, β -relaxation is found to be strongly dependent on the chain length in linear poly(glycidyl phenyl ether) in contrast to what happens in cyclic chains. This behaviour is attributed to the specific contributions of the chain-ends to the β -relaxation; a fact that can be used to detect the presence of linear contaminants in cyclic polymers.

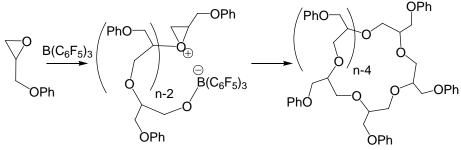


Figure 1. Cyclic poly(glycidyl phenyl ether) obtained by zwitterionic ring-opening polymerization.¹

(1) Asenjo-Sanz, I.; Veloso, A.; Miranda, J. I.; Pomposo, J. A.; Barroso-Bujans, F. Polym. Chem. 2014, 5, 6905.

(2) Asenjo-Sanz, I.; Veloso, A.; Miranda, J. I.; Alegria, A.; Pomposo, J. A.; Barroso-Bujans, F. *Macromolecules* **2015**, *10.1021/acs.macromol.5b00096*.