ROP OF VIC-DISUBSTITUTED LACTONES: A DIASTEREOSELECTIVE WAY TO POLYMERIZE

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For this work, at first we have studied the acid catalysed lactonization of several γ-hydroxyesters, bearing methyl substituents at different positions. A 1H-NMR kinetic study of this set of monomethyl and/or gem-dimethyl substituted esters in CDCl₃ was carried out. We evaluated the effect of the leaving group (ethyl vs. i-propyl ester) and the catalyst efficiency. We found that i) a monomethyl substitution produces a lowering of the energy barrier similar to that of a gem-dimethyl substitution (Thorpe–Ingold effect), ii) the ring closure of i-propyl esters is slower than that of ethyl esters, iii) strong acids are more efficient than weak acids according to the Brønsted relationship, and iv) the Thorpe–Ingold effect is not just an intrinsic feature of the linear precursor but it depends on the catalyst as well.[1,2] Now, we would like to give an explanation and clarify three issues: i) how is the cyclization affected by the vicinal substitution? ii) is the effect stereospecific, that is to say, dependent on the diastereomeric relation (syn or anti) between the two vicinal substituents? iii) is it possible to observe a stereospecific effect in the Ring Opening Polymerization (ROP) of lactones as well? Preliminaries studies on model compounds indicate that the vic-disubstituent effect is not only stereospecific, since the anti linear precursors undergo to the cyclisation reaction much faster than the corresponding syn diastereoisomers, but it is more efficient than the above mentioned Thorpe-Ingold effect. Indeed, the anti vicinal substituted adduct is faster than the gem-disubstituted of about 4 times in the lactonization reaction.

Interesting results are obtained in the ROP process too, in which vic-disubstituted d-lactones show a stereospecific polymerization (in a ratio of around 1 to 6), dependently of the diastereomeric configuration of the monomer.