

2-OXEPANE-1,5-DIONE: A PRECURSOR OF A NOVEL CLASS OF VERSATILE SEMICRYSTALLINE BIODEGRADABLE (CO)-POLYESTERS.

Philippe Lecomte^{1,*}, Jean-Pierre Latere Dwan'Isa^{1,2},
Philippe Dubois^{1,3}, Robert Jérôme¹

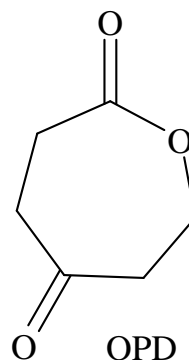
¹Center for Education and Research on Macromolecules (CERM),
University of Liège, Sart-Tilman, B6a, B-4000 Liège (BELGIUM)
<http://www.ulg.ac.be/cerm>

(Research Center in Science of Polymeric Materials (CRESMAP))

²Present address: Composite Materials and Structures Center Michigan State
University East-Lansing, MI 48824 (USA)

³Present address: Laboratory of Polymeric and Composite Materials (SMPC),
University of Mons-Hainaut, Place du Parc, 20, B-7000 Mons (BELGIUM)

2-oxepane-1,5-dione (OPD) was synthesized by Baeyer-Villiger oxidation of 1,4-cyclohexanedione and ring-opening polymerized by 1-phenyl-2-propanol / tin octoate with formation of a semicrystalline polyester of high melting temperature (T_m : 147°C). A crystallographic study showed that the polyester is orthorhombic in the P212121 space with two molecules extended along the c-axis as is the case for poly(ϵ -caprolactone) (PCL).



Dibutyltin dimethoxide and 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP) proved to be efficient initiators for the random copolymerization of ϵ -caprolactone (ϵ CL) and OPD. Random distribution of the comonomer units was confirmed by DSC, ^1H and ^{13}C NMR analyses. A single T_m was observed, which varies regularly and monotonically with the OPD content as result of a cocrystallisation phenomenon. The single glass transition temperature (T_g) obeys the Fox equation.

It is noteworthy that a copolymer containing 30 mol % OPD exhibits a T_m of 90°C. It is stable up to 140°C under nitrogen for one hour, such that processing by extrusion is quite possible. The OPD decomposition is maximum at 223°C for a heating rate of 10°C/min. The mechanism of thermal degradation was investigated and cleared up. The ketone increases the copolymer hydrophilicity and thus sensitivity to hydrolysis. The mechanical properties are quite reminiscent of PCL of comparable molecular weight. Quite interestingly, OPD imparts sensitivity to photo-cross-linking to this novel class of materials.