# 2-Oxepane-1,5-dione: A Precursor of a Novel class of Verstaile Semicrystaline Biodegradable (Co)polesters. 

Jean-Pierre Latere Dwan'Isa ${ }^{1,2}$, Philippe Lecomte ${ }^{1}$, Philippe Dubois ${ }^{1,3}$, Robert Jérôme ${ }^{1}$
${ }^{1}$ Center for Education and Research on Macromolecules (CERM),
University of Liège, Sart-Tilman, B6, B-4000 Liège (BELGIUM)
http://www.ulg.ac.be/cerm
(Research Center in Science of Polymeric Materials (CRESMAP)
${ }^{2}$ Present address: Composite Materials and Structures Center Michigan State University East Lansing, MI 28824 (USA)
${ }^{3}$ Present 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 $\left(\mathrm{T}_{\mathrm{m}}: 147^{\circ} \mathrm{C}\right)$.


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

It is noteworthy that a copolymer containing $30 \mathrm{~mol} \% \mathrm{OPD}$ exhibits a $\mathrm{T}_{\mathrm{m}}$ of $90^{\circ} \mathrm{C}$. It is stable up to $140^{\circ} \mathrm{C}$ under nitrogen for one hour, such that processing by extrusion is quite possible. The OPD decomposition is maximum at $223^{\circ} \mathrm{C}$ for a heating rate of $10^{\circ} \mathrm{C} / \mathrm{min}$. 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.

