2-Oxepane-1,5-dione: A Precursor of a Novel class of Versatile Semicrystalline Biodegradable (Co)polyesters.

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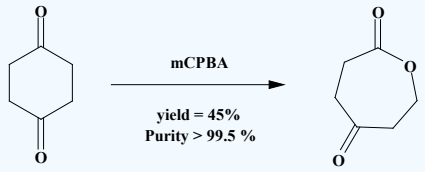
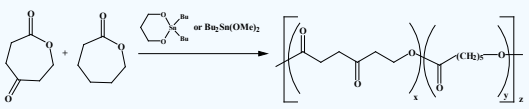
Synthesis of 2-oxepane-dione (OPD)

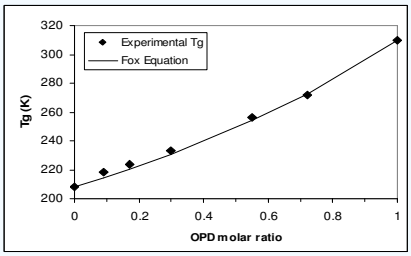


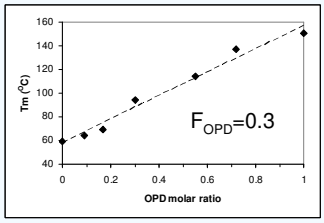
OPD and εCL Copolymerization



Sn(IV) alkoxides are very efficient initiators.
$Al(OiPr)_3$, $Y(OiPr)_3$ are not suitable because of detrimental complexation of the initiator to the C=O group of the OPD units

Thermal properties : P(OPD-co-εCL), a semicrystalline copolymer





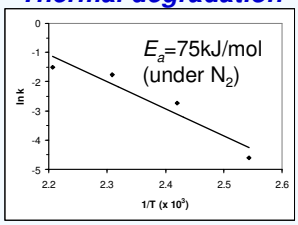
Cell parameters (Å)	PCL	P(OPD)
A	7.49	6.80
B	4.98	5.18
C	17.05	17.17
£	6.2	6.2
δ	2.98	2.82

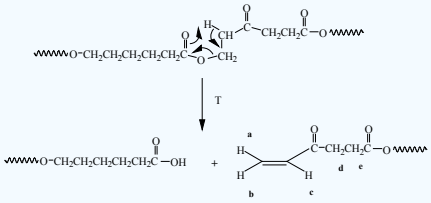
Regular and continuous increasing T_m

PCL and P(OPD) units are isomorphous

P(OPD-*co*-εCL) containing 30 mol% OPD exhibits a T_m = 90°C, which opens up new opportunities for applications that require a higher service temperature than PCL, i. e., packaging applications

Thermal degradation : sample : P(OPD-co-εCL) ; F_{OPD}=0.3





k (%/min) determined by Isothermal TGA

Degradation of P(OPD-*co*-εCL) is faster than PCL (E_a=92kJ/mol) because of the ketone group of the OPD units

P(OPD-*co*-εCL) containing 30 mol% of OPD is stable up to 140°C under nitrogen for one hour, such that processing by extrusion is possible.

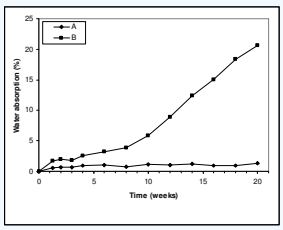
Mechanical properties

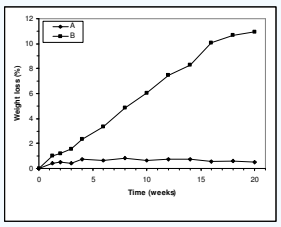
Copolymer	Mn (K)	ε_b (%)	σ_b (MPa)	σ_y (MPa)
P(OPD-co-OPD), F_{OPD}=0.33	42	800	26	15
CAPA 650	50	1000	36	13
		Impact energy (kJ/m²)		
P(OPD-co-OPD), F_{OPD}=0.34	33K	18-20		
P(OPD-co-OPD), F_{OPD}=0.33	42K	No breaking		
P(OPD-co-OPD), F_{OPD}=0.33	50K	No breaking		

Above a critical molecular weight, the tensile and impact properties are comparable to those ones of commercially available PCL (CAPA, Solvay)

Hydrolytic degradation

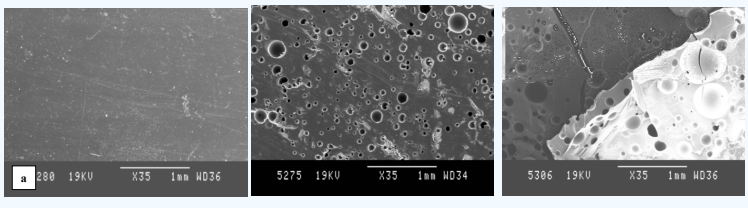
Conditions : pH=7.4 at 37°C ; P(OPD-*co*-εCL) (Mn=35000 ; 30 mol% of OPD)





A = PCL ; B= P(OPD-*co*-εCL)

SEM image after immersion



After 0 days **After 9 days** **After 20 weeks**

The C=O group imparts higher hydrophilicity, which has a key role in the increase of the hydrolytic degradation rate compared to PCL

Crosslinking under UV

Exposure of P(OPD-*co*-εCL) (F_{OPD}=0.3) to UV induces loss of solubility. Frequency sweep experiments show higher elasticity above T_m. An increased brittleness was shown by tensile properties. No significant effect on T_m and ΔH_m was observed. The C=O group of the OPD units is at the origin of this behavior.

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