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**Acid Catalyzed Polymerization of Macrolactones in Bulk and Aqueous
Miniemulsion: Ring Opening vs. Condensation**

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Abstract

Aliphatic polyesters from three macrolactones (pentadecalactone, globalide and ambrettolide) were synthesized by organic acid catalyzed polymerization in bulk and in an aqueous miniemulsion. Two different mechanism of polymerization take place depending on the polymerization media. Relatively high molecular weight polyesters (M_n aprox. 10000 $g\ mol^{-1}$) were obtained in bulk following a ring opening polymerization mechanism. Interestingly, relatively fast polymerizations were observed which depended in the acid PKa (triflic acid > benzene sulphonic acids > diphenyl phosphate). On the other hand, a condensation mechanism is observed in water miniemulsion leading to oligoesters of aprox. 2000 g/mol. This molecular weight limitation prevented these latexes to be suitable for most applications. Interestingly, it is demonstrated that the introduction of unsaturated macrolactones in these aqueous latexes allows subsequent cross-linking leading to cured polyester films.

Keywords: organic catalysis, ring opening polymerization, macrolactones, miniemulsion.

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