SYNTHESIS OF NEW SUBSTITUTED POLYCAPROLACTONES
BY RING-OPENING POLYMERIZATION

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Nowadays, a steadily increasing attention is paid to the synthesis of aliphatic polyesters, e.g. poly(ε-
ocaprolactone) and polylactides. Their remarkable properties of biodegradability and biocompatibility pave indeed the way to many new applications not only in the biomedical field but also as substitutes for nondegradable polymers, e.g. packaging. So aliphatic, polyesters with improved and/or original properties are highly desirable.

A general strategy shown below relies on the synthesis of ε-caprolactone substituted by well-defined functional group (protected or not) in γ-position (S) followed by Ring Opening Polymerization (ROP) initiated by aluminum alkoxides ROAlEt$_2$. The well-known living / controlled character of this ROP is essential to the tailoring of macromolecules with narrow molecular weight distribution and predictable molecular weight. A wide range of architectures can be made in line with a real "macromolecular engineering".

![Chemical structure](image)

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\begin{align*}
\text{ROH} & \xrightarrow{\text{Et$_3$Al}} \text{ROAlEt$_2$} \quad \text{S = H, functional pendant group (protected or not)} \\
& \xrightarrow{\text{toluene, rt}} \text{RO} \quad \text{R = (protected) functional group or not, polymeric or not}
\end{align*}
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In the first part of the lecture, a general overview will be presented with a special emphasis on our more recent experimental results. A particular attention will be paid to the synthesis of amphiphilic polyesters.

The second part of the lecture will deal with a strategy able to extend the range of polycaprolactone containing materials; i.e. combination of ROP with other living / controlled polymerization techniques such as Stable Radical Free Polymerization (SRFP), Atom Transfer Radical Polymerization (ATRP) and Ring Opening Metathesis Polymerization (ROMP). Representative examples will be discussed.