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**AVANCES EN MATERIALES POLIMÉRICOS**  
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## RING OPENING POLYMERIZATION OF MACROLACTONES USING AMINES AS INITIATORS

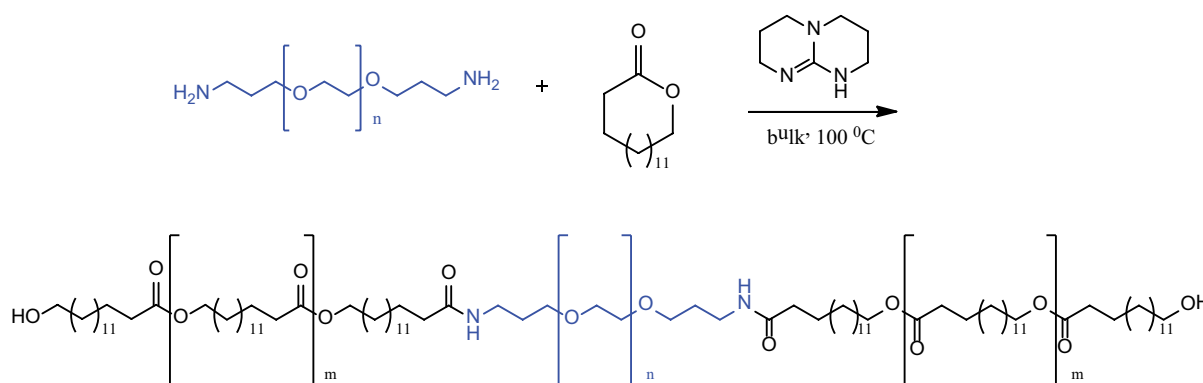
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More and more attention has been paid to the synthesis of aliphatic polyesters which are a kind of degradable and biocompatible materials useful in medical, pharmaceutical and environmental applications [1]. Among these polyesters, poly( $\omega$ -hydroxy fatty acid) family could be obtained from biobased feedstock. Poly( $\omega$ -pentadecalactone), prepared from the commercially available  $\omega$ -pentadecalactone (PDL), displays good mechanical properties comparable to high density polyethylene (HDPE) [2]. On the other hand, the macrocycle  $\omega$ -6-hexadecenlactone (6HDL) is used in the fragrance industry with a worldwide volume of around one metric ton per year [3]. The ring opening polymerization (ROP) of these macrolactones mediated by alcohols as initiators and organic and metal-based catalysts has been reported before with satisfactory results [4,5]. In the present work, the polymerization of these macrolactones has been studied using amines as initiators.

The ROP of both PDL and 6HDL was carried out in bulk at 100 °C using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as organocatalyst. Distinct types of amines were tested as initiators for the ROP of these macrolactones. The copolymerization reaction was also studied by ROP of PDL and 6HDL with an oligo-polyethylene glycol bis(3-aminopropyl) terminated and an amino-ended homopolymer (poly( $\gamma$ -benzyl  $\alpha$ ,L-glutamate) as initiator.

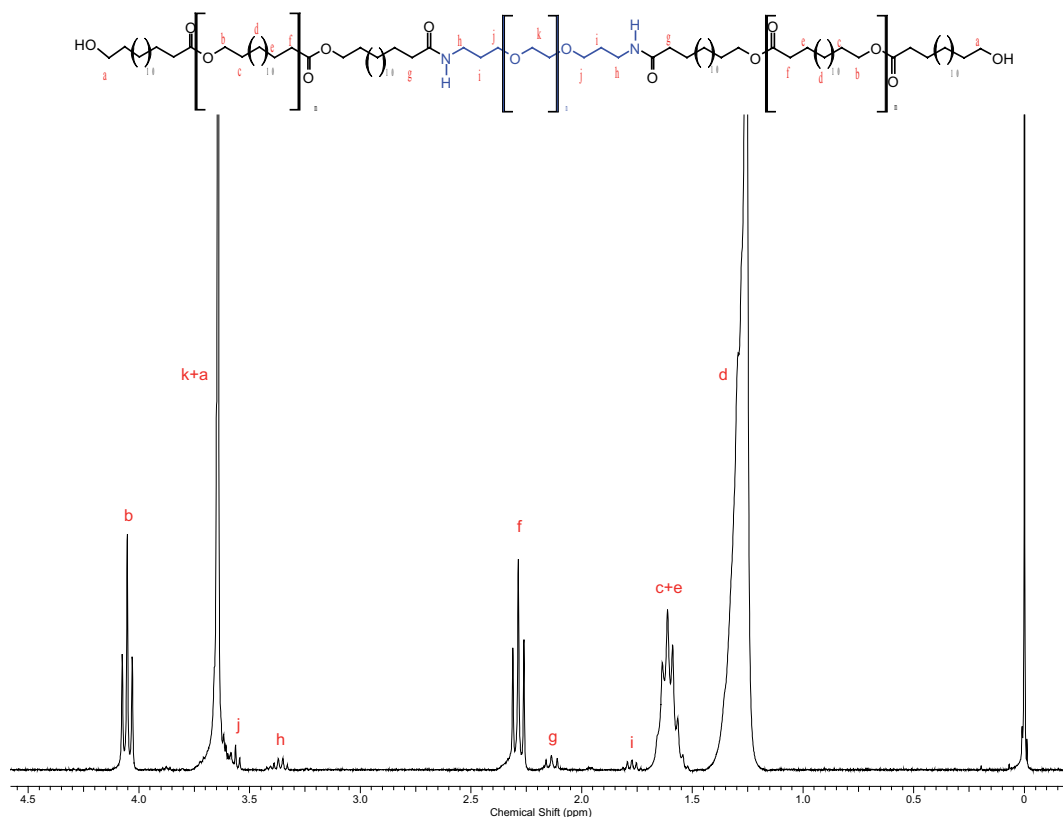
An illustrative reaction system for the ROP of the PDL is shown in Fig. 1



**Fig. 1.** Ring Opening Polymerization of PDL by poly(ethylene glycol) bis(3-aminopropyl) terminated as initiator and TBD as catalyst.

The organocatalyst/initiator system TBD/RNH<sub>2</sub> (where RNH<sub>2</sub> is either a monoamine or a diamine) proved to be an efficient system to promote the ROP of PDL and 6HDL. The homopolymers and the copolymers were characterized by <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy. Fig. 2 shows the <sup>1</sup>H-NMR spectrum of the PPDL-co-PEG copolymer obtained using PEG bisamino terminated as initiator.

Increasing the catalyst:initiator ratio from 1:1 to 5:1 resulted in a significant increase in the polymerization rate and almost full conversion could then be reached. Representative results for the polymerization of PDL are reported in the Table 1.



**Fig. 2.** <sup>1</sup>H-NMR spectrum (300 MHz, CDCl<sub>3</sub>, RT) of PPDL-co-PEG

**Table 1.** Ring Opening Polymerization of ω-pentadecalactone mediated by amines and TBD.

Initiator	[PDL]/[Cat]/[Ini]	Reaction Time (h)	Conv (%)	Mn (g/mol)
	[10]/[1]/[1]	96	64	1780
	[10]/[5]/[1]	3	99	2860
	[20]/[5]/[1]	3	99	5700
	[20]/[5]/[1]	3	-	-

Preliminary experiments have shown that ROP of PDL seems to take place also when a polypeptide is used as initiator; nevertheless the copolymerization of both PDL and 6HDL is still under research.

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