

# (Bis)pyrazole Zinc And Copper Complexes As Catalysts For Ring Opening Polymerization Of Lactones/Lactides

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## ABSTRACT

A series of pyrazolyl carboxylate Zn(II) and Cu(II) complexes was synthesized and different structures were obtained for the complexes. The efficiency of these compounds towards catalysing the ring opening polymerization (ROP) of lactides and lactones was evaluated and all the compounds analysed showed catalytic activities. In-depth kinetic studies were carried out and the ROP showed living characteristics.

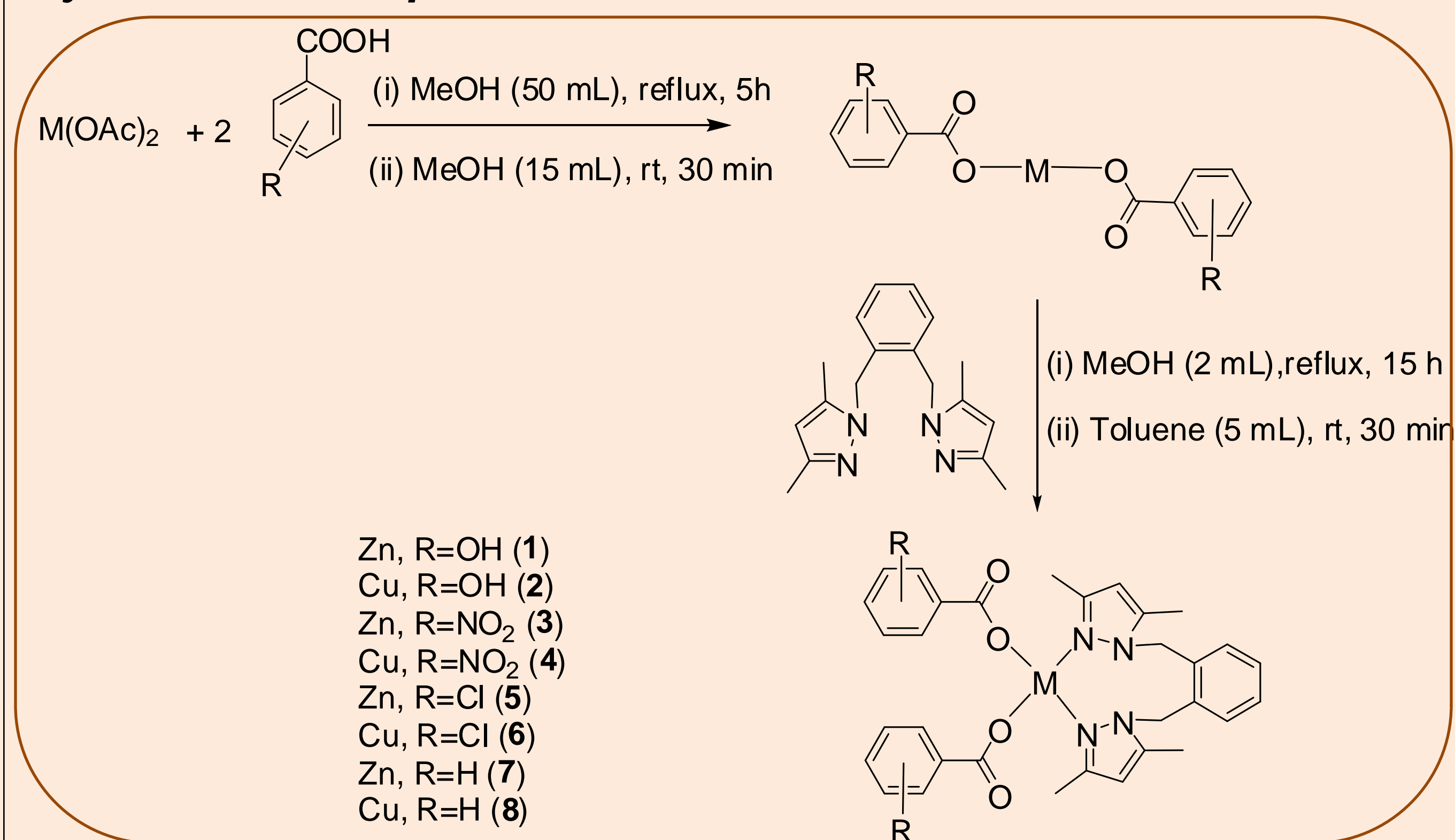
## INTRODUCTION

Recently, biodegradable polymers have been attracting considerable attention due to their potential application in human life [1a]. Among them, the aliphatic polyesters, such as poly( $\epsilon$ -caprolactone) (PCL) and polylactide (PLA) show their potential applications in the agricultural, packaging and medical fields due to their biodegradable, biocompatible, and permeable properties [1b].

Metal complexes have been extensively used as catalysts for the ring opening polymerization (ROP) of lactides [2a] and lactones [2b]. These catalysts usually feature a metal-oxygen bond, which has been shown to be the point of attack by the lactide and lactone [3]. Thus, the synthesis of zinc(II) and copper(II) complexes and their application as catalyst for ROP of D,L-lactide and  $\epsilon$ -caprolactone will be reported in this paper.

## RESULTS & DISCUSSION

### •Synthesis of complexes



Scheme 1. One pot reaction for the synthesis of complexes

### •X-ray structures of complexes

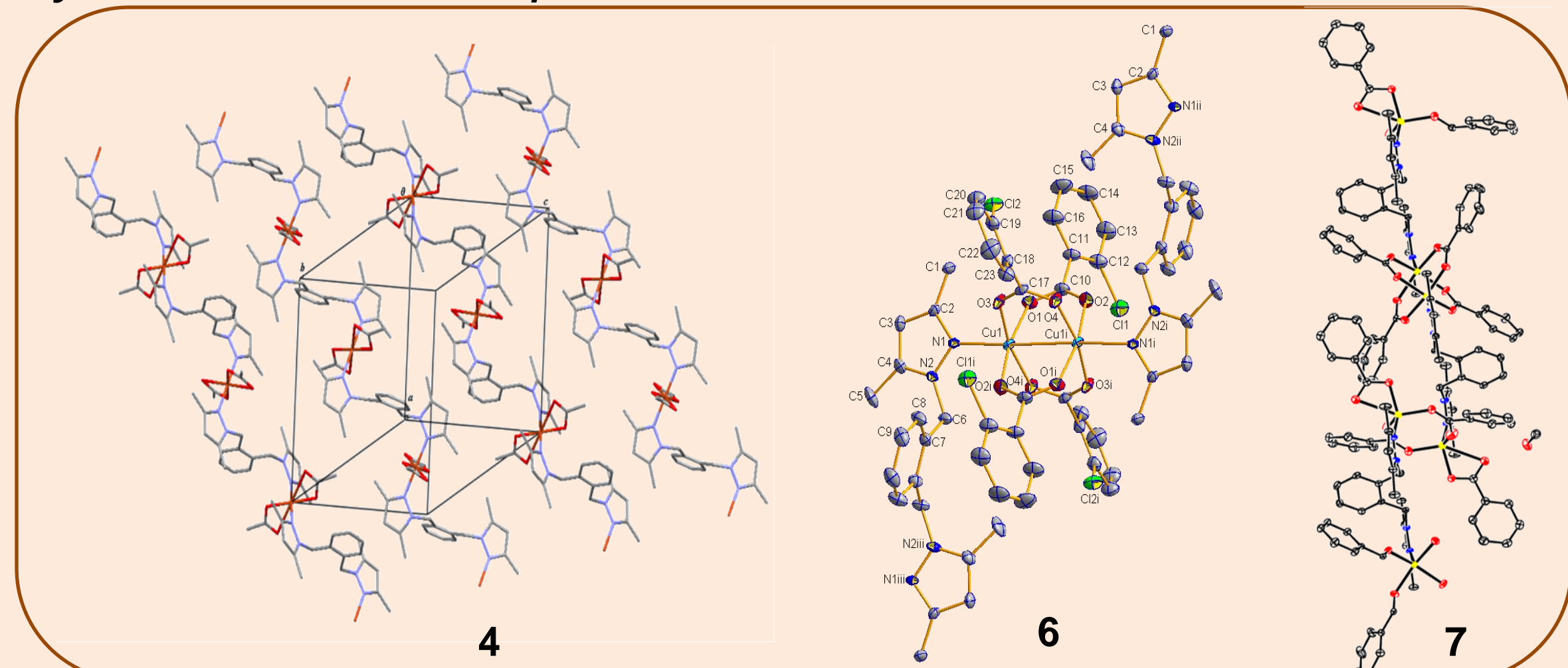
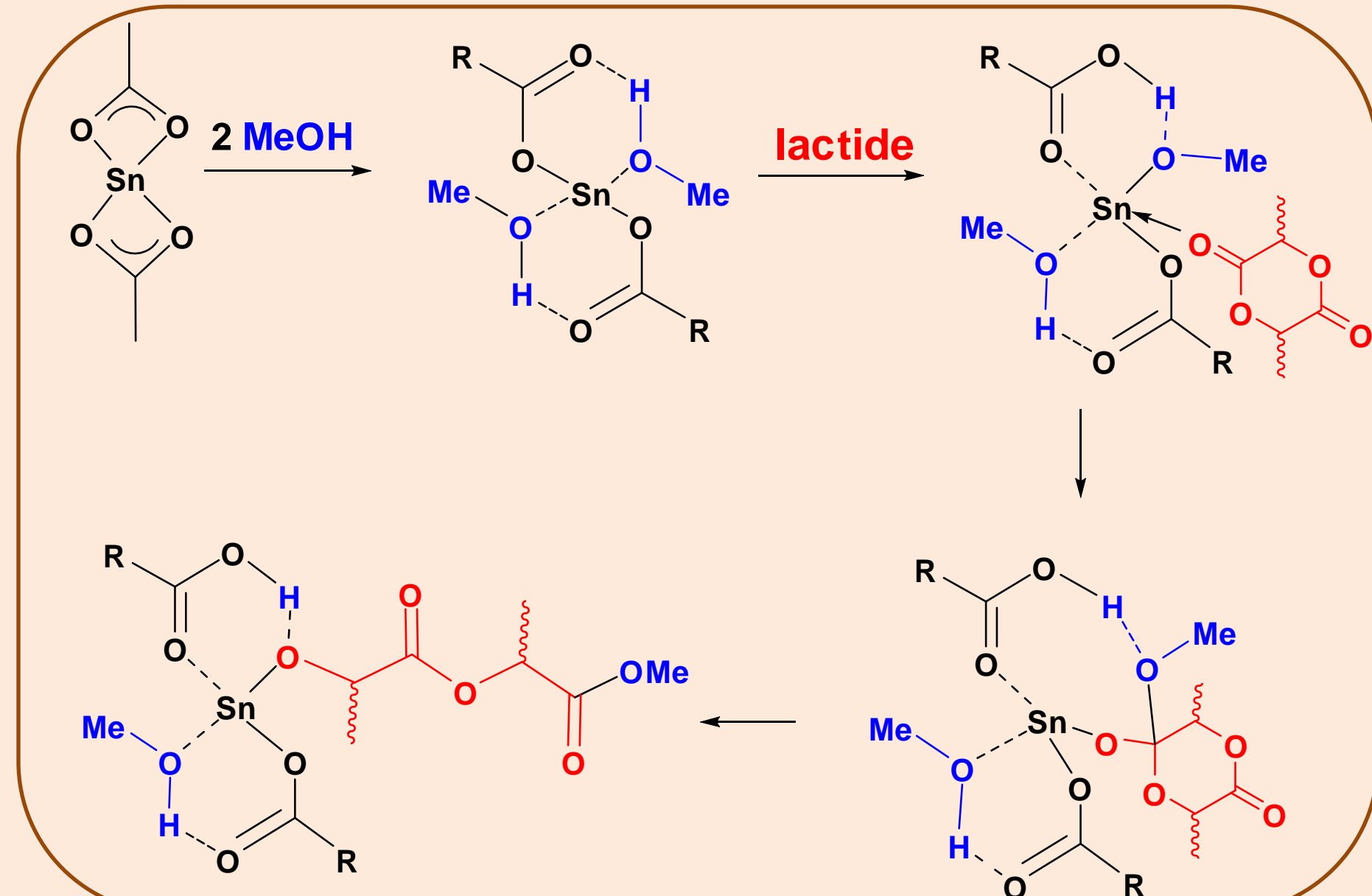


Figure 1. Structures of complexes 4, 6 & 7

### •Ring opening polymerization of $\epsilon$ -caprolactone & D,L-lactide



Scheme 2. Accepted mechanism for the effect of MeOH on the coordination-insertion polymerization of lactide [4]

### •Characterization of polymers

Table 1.  $M_n$  for PCL & PLA synthesized using complexes 1-8 as catalysts

Complex	$\epsilon$ -Caprolactone, [M]/[I]=50, Bulk, 110°C		D,L-lactide, [M]/[I]=100, Toluene, 110°C	
	Conv (%)	$M_n^c$	Conv (%)	$M_n^c$
1	93	4440	97	1900
1 <sup>a</sup>	71	2053	-	-
1 <sup>b</sup>	-	-	62	924
2	92	3160	100	2953
3	94	4101	96	2108
4	100	2594	96	1812
5	100	5563	97	2307
6	96	3092	91	1877
7	73	3531	96	2350
8	98	4066	97	1695

<sup>a</sup>  $\epsilon$ -Caprolactone polymerization using [M]/[I]=3333; <sup>b</sup> D,L-lactide polymerization, with methanol as additive; <sup>c</sup>  $M_n$  determined from <sup>1</sup>H NMR spectra; Complexes 2, 6 & 8 are bimetallic and 4 & 7 are polymeric.

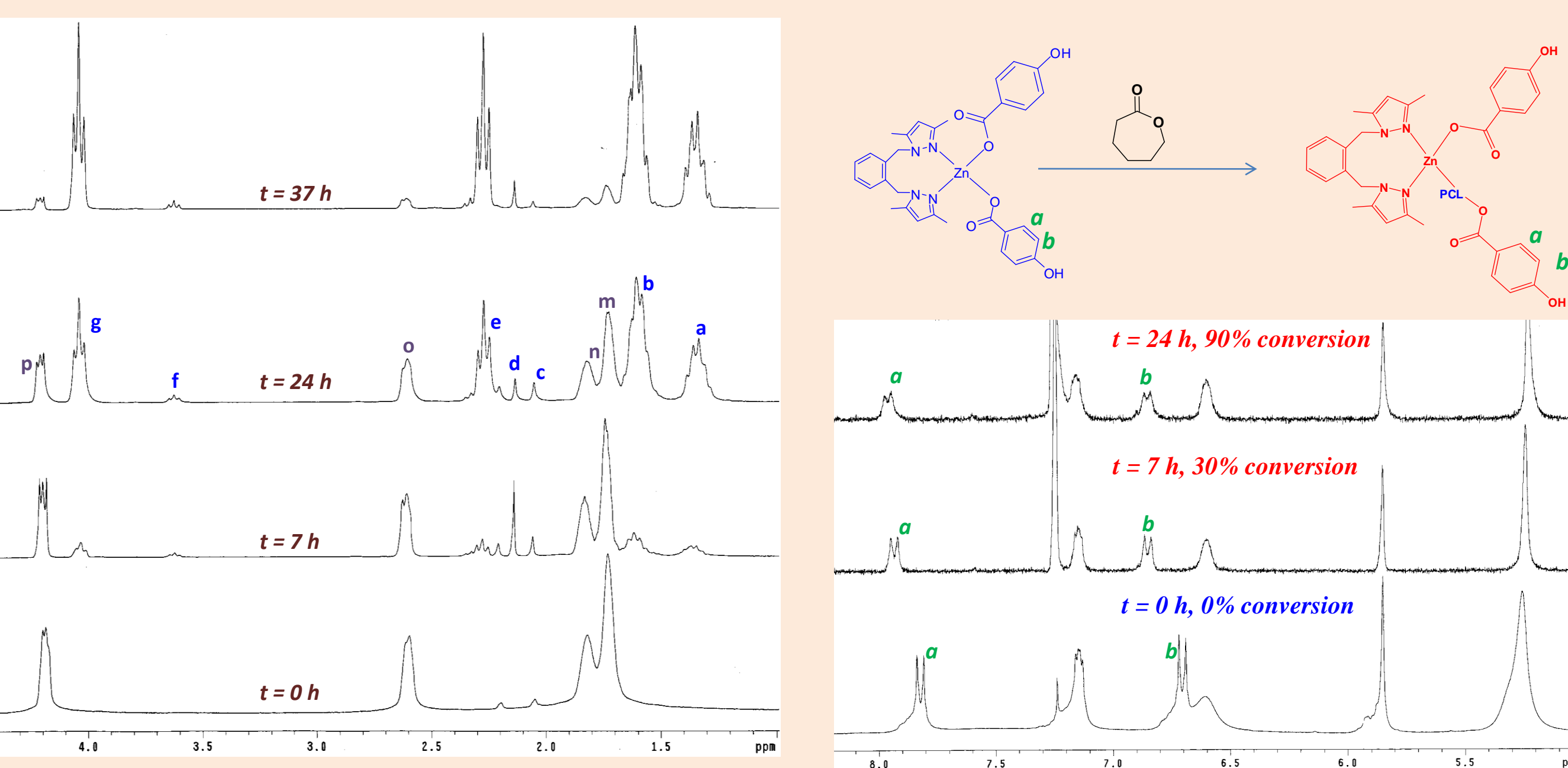
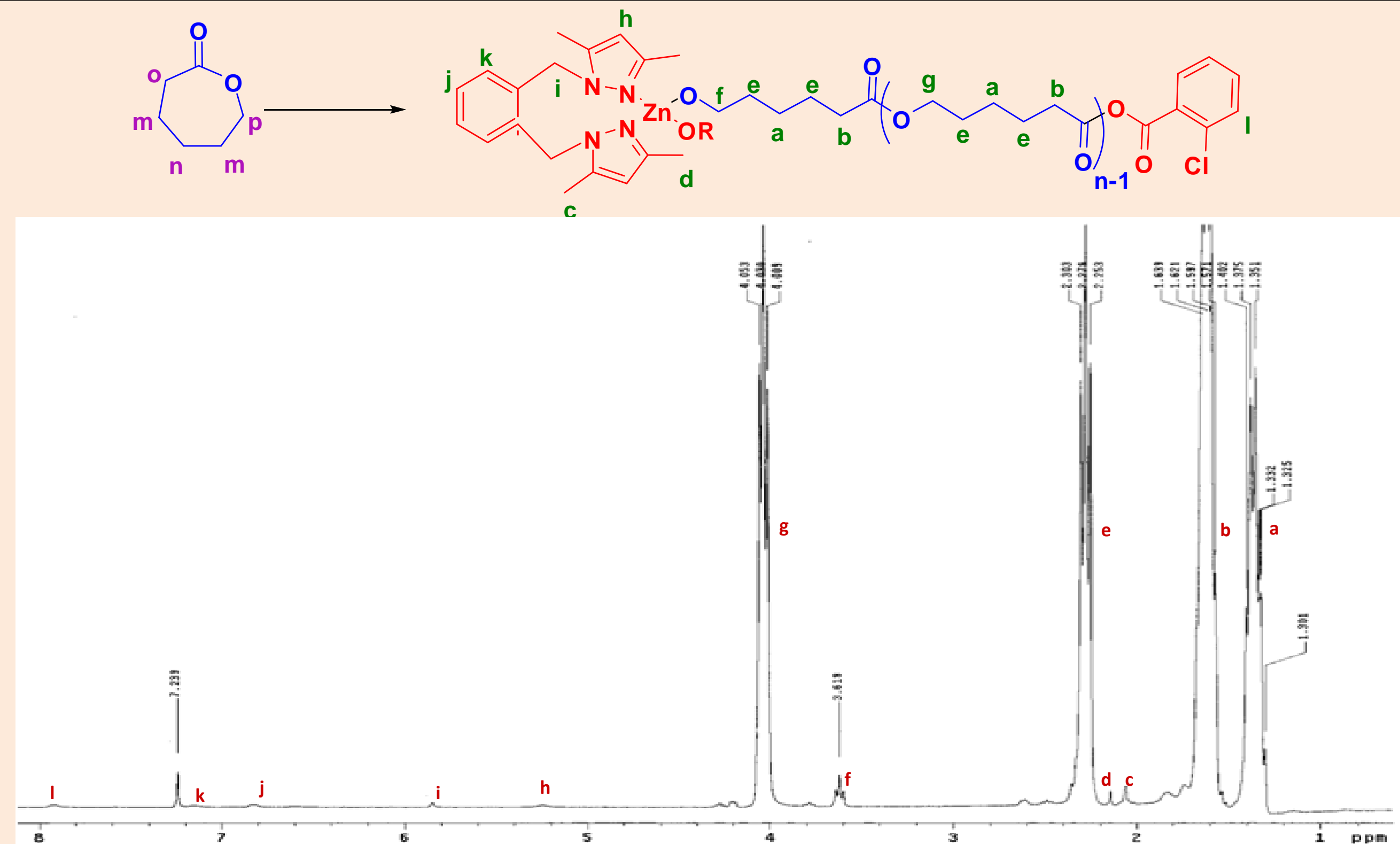
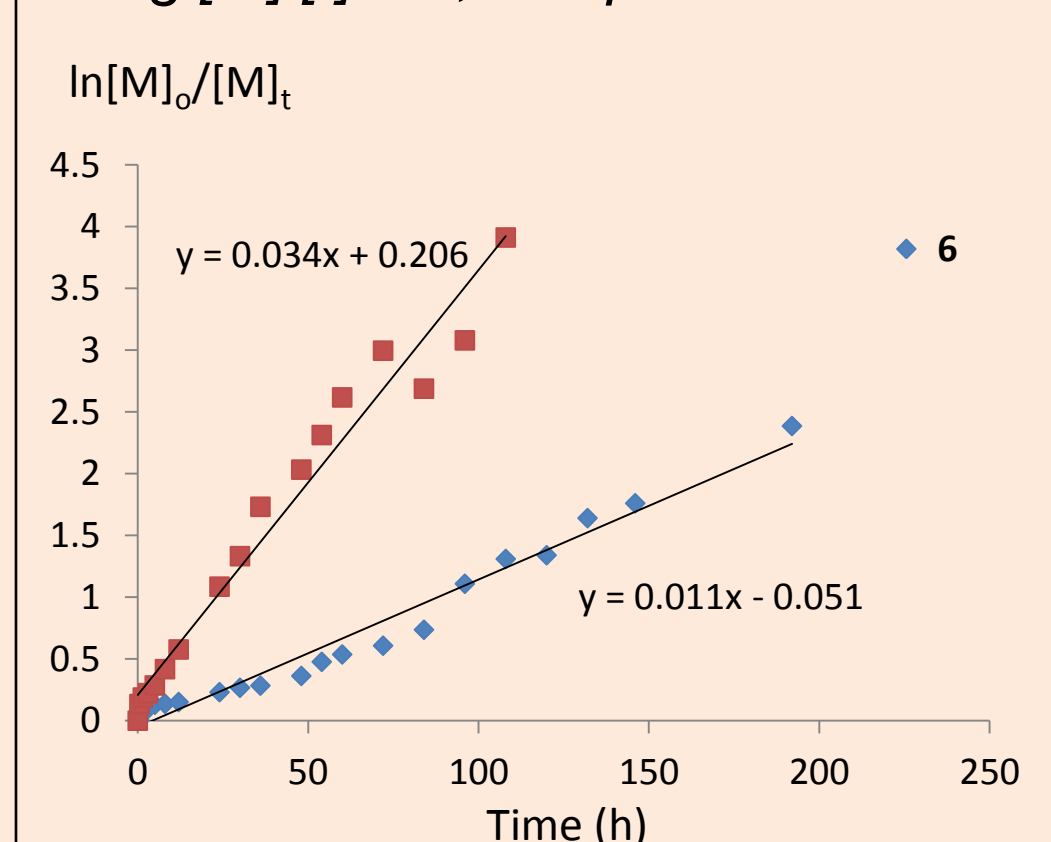
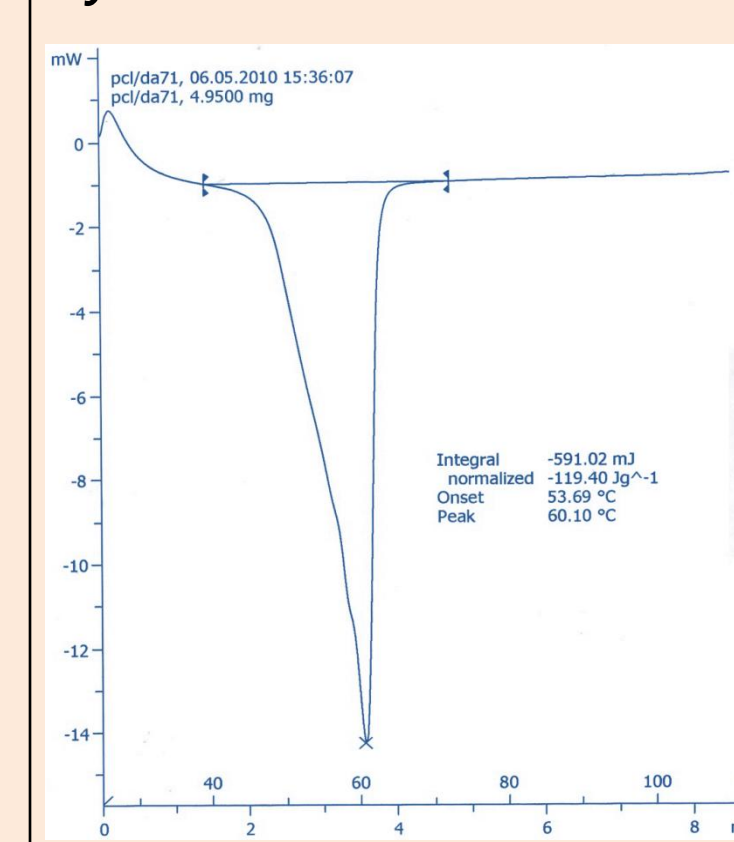


Figure 2. <sup>1</sup>H NMR spectra of polymer mixture

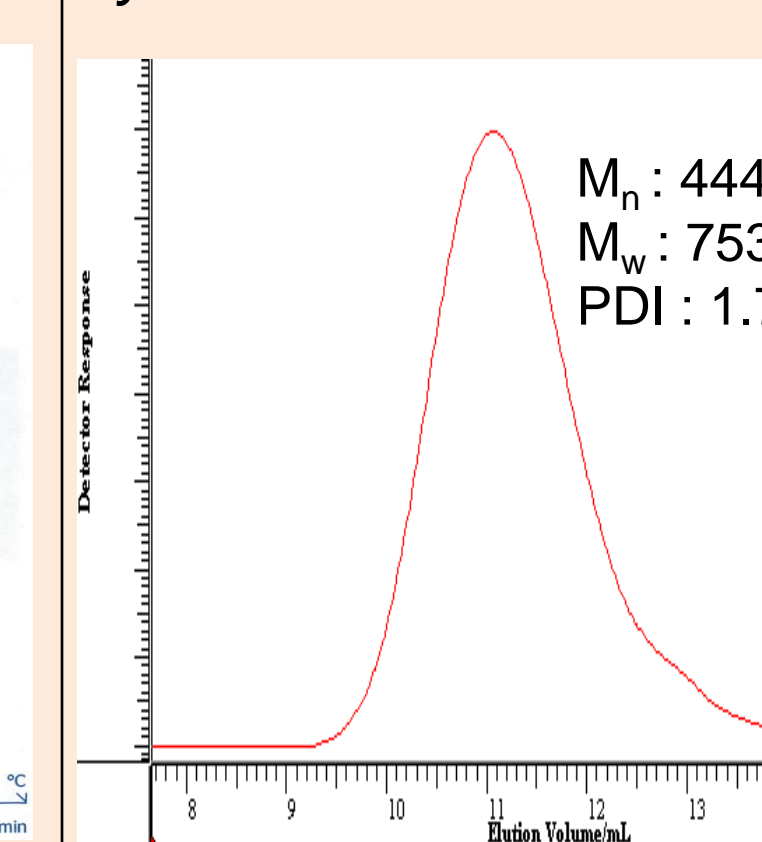
### Kinetic plot for ROP of $\epsilon$ -caprolactone using [M]/[I]=50, complexes 6 & 7



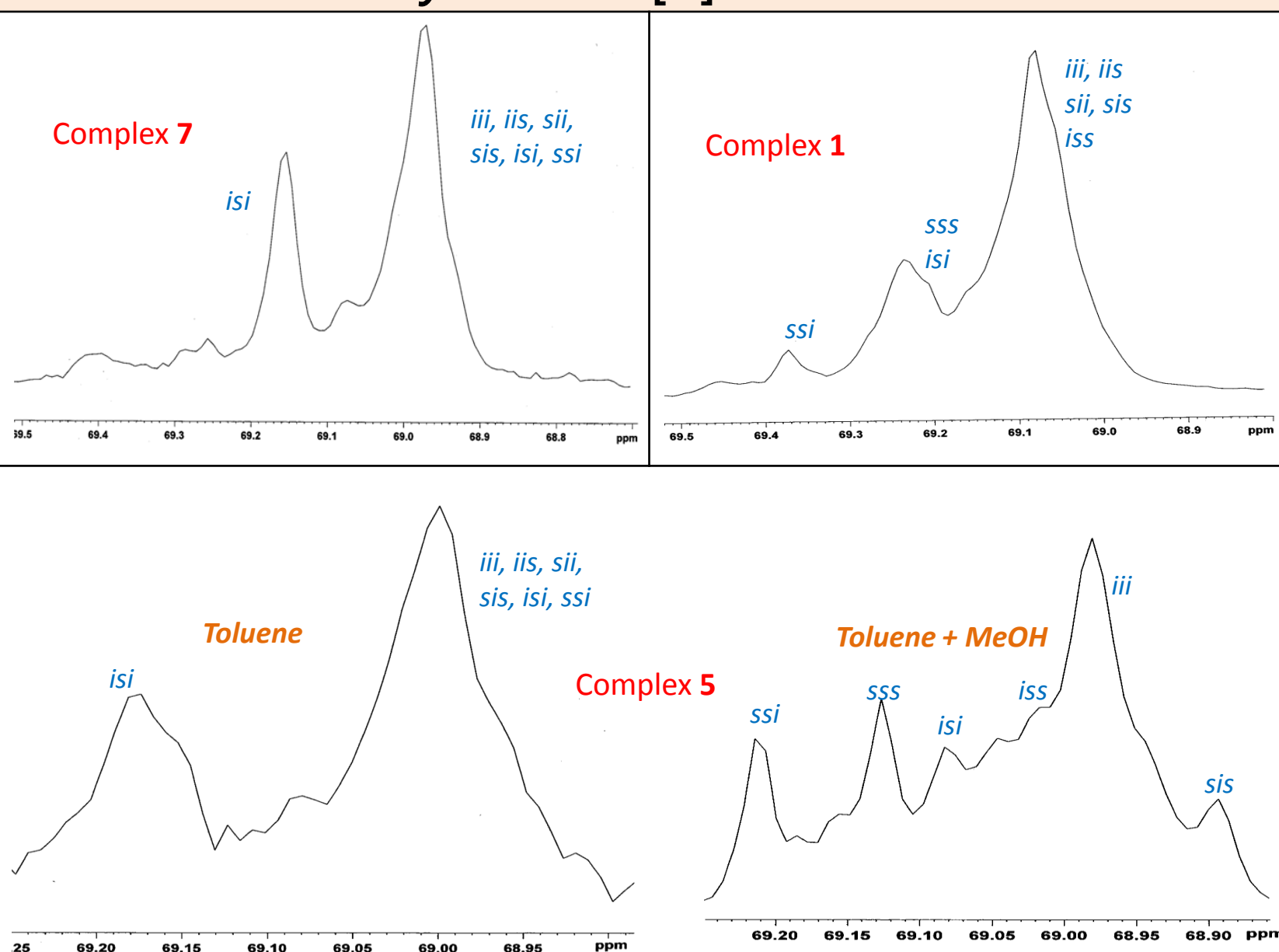
### DSC of PCL synthesized by 5



### SEC of PCL synthesized by 1



### Stereochemistry of PLA [5]



Conv (%)	<sup>13</sup> C NMR characterization			
	Tetrad intensities (%)			
	iii,iis,si	isi	sss	iss
	75	25	0	0
	50	50	0	0
	50	12.5	12.5	12.5

## CONCLUSION

A series of Zn(II) and Cu(II) pyrazolyl carboxylate complexes was synthesized and all the compounds showed some catalytic properties when used as initiator for the ring opening polymerization of lactones and lactides under various conditions. The complexes gave different activities and the polymers obtained were different in terms of stereochemistry as well. Zn complexes were better catalysts than their copper analogues and  $\epsilon$ -caprolactone ring opens more readily than D,L-lactide ring. The use of methanol as additive helps to speed up the polymerization process, but affects the stereochemistry of the polymers formed.

## ACKNOWLEDGMENT

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