

Polymerization of β -propiolactone via nickel-chelate complexes

Study of the initiation process by ^1H NMR spectroscopy

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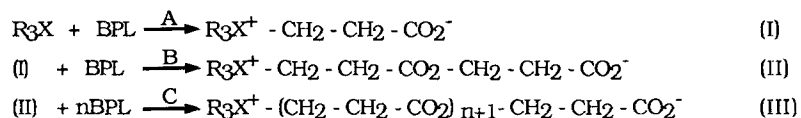
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SUMMARY

The polymerization of β -propiolactone, initiated by nickel propionate-tributylphosphine was studied in toluene at 35°C. Monomer and initiator consumptions were followed by ^1H NMR spectroscopy. The spectra were recorded at regular intervals and show that: (1) The phosphorus-chelated nickel complex is destroyed; (2) the resulting nickel carboxylate creates a new complex with the lactone. (3) The length of this transfer period depends on the initial monomer concentration. (4) The "activated" lactone leads to the formation of a zwitterion with consumption of tributylphosphine. (5) The zwitterion reacts with complexed lactone to give a β -substituted carboxylate.

INTRODUCTION

In several anionic and cationic polymerizations initiated by uncharged Lewis bases the formation of zwitterions in the initiation process has been postulated (1-7). For example, anionic polymerization of β -propiolactone (BPL) initiated by tertiary amine and phosphine leads to the formation of macrozwitterion according to the following three elementary reactions (7):

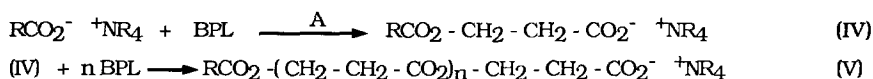


Scheme 1

The crucial and rate-determining step in this process of producing zwitterionic poly β -lactones seems to be reaction B (8,9).

Starting from tetraalkylammonium carboxylate, Hall showed that this initiator attacks the β -propiolactone (BPL) to give the β -substituted carboxylate which in turn attacks further monomer molecules to cause chain growth (10).

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Scheme 2

In this case the carboxylate plays the role of the nucleophilic moiety and no formation of zwitterion occurs.

Using a novel class of catalyst, metal acetate-tri-n-butylphosphine system, Tani et al. realized a stereoselective polymerization of γ -benzyl l-glutamate N-carboxyanhydride (11). These authors were able to demonstrate that the high catalytic activity of the $\text{Ni}(\text{OAc})_2$, $n\text{PBu}_3$ could be correlated with the nature of the metal ion.

Experimental results from our laboratory (12) on the polymerization of β -propiolactone using both the tributylphosphine and the nickel propionate-tributylphosphine have shown that the tributylphosphine when alone initiates the polymerization at a rate much slower than when in the complex. It was also reported that the length of the induction period depends on the ratio $[\text{monomer}]/[\text{Ni complex}]$, but the variation of k_i values with monomer concentration suggests that the mechanism is not a simple one as far as the reaction order is concerned. Moreover from these experimental data it was not clearly established that the polymerization proceeds via a zwitterionic polymerization mechanism. In order to understand the role played by the nickel atom in the initiation process, the polymerization of β -propiolactone initiated by nickel propionate-tributylphosphine catalyst system was followed by NMR. The use of the NMR technique allows us to follow the consumption as well as the appearance of the different molecules during the reaction, and to check if the polymerization initiated by the complex is of zwitterionic type.

EXPERIMENTAL PART

Nickel propionate was synthesized by a general procedure using the silver salt of the corresponding acid and NiCl_2 (13). Tributylphosphine complex of nickel carboxylate was prepared according to the method of Jensen (14). For example, nickel propionate (2mM) and tributylphosphine (4mM) were added to 1mL of methanol giving a red solution. This solution was kept for two days at -30°C for crystallisation. The red crystals obtained were then isolated by filtration, washed twice with cold methanol (-30°C). The corresponding anhydrous complex was obtained by heating the hydrate complex in vacuo at 30°C .

The complex is soluble in toluene and gives a red solution. The NMR spectra show that the complex is stable several days in this solvent.

NMR samples of β -propiolactone, and nickel propionate-tributylphosphine complex were prepared by dissolving the compounds at -10°C in 0.3 ml of toluene- D_8 under a nitrogen atmosphere and the NMR tubes were sealed.

Magnetic resonance measurements were carried out at 200.13 MHz using a BRUKER AC 200 equipped with an Aspect 3000 computer and a ^1H selective probe. For polymerization studies the probe was regulated at 35°C (± 1). The results of the two polymerizations shown in this paper were obtained in a toluene solution with 10 or 0.16 ML^{-1} of lactone and 0.02 ML^{-1} of complex. The paramagnetic nickel atom interacts with the organic molecules to give broad resonances, thus a concentration of 0.02 ML^{-1} in complex was added giving a good compromise to obtain rapidly a spectrum without loss in resolution.

^1H spectra were recorded at regular intervals during the polymerization to control both the evolution of the species and the appearance of new

molecules. The chemical shifts were initially referenced to tetramethylsilane (TMS).

RESULTS

A first polymerization was followed at lactone and complex concentrations of 10 ML⁻¹ and 0.02 ML⁻¹ respectively. The chemical shifts values of signals corresponding to the different compounds present during the polymerization are displayed in table 1. At time t=0 signals for the complexed phosphine were observed at 1.02 1.5-1.7 and 1.84 ppm. Assignment of these resonances was achieved using the selective irradiation technique. The signals corresponding to the β -propiolactone protons are observed at 2.65ppm (α position to the CO group) and 3.4 ppm.

TABLE 1: Chemical shifts values of signals corresponding to the different compounds present during the polymerization (solvent:toluene, $\theta=35^{\circ}\text{C}$)

Phophine	P-CH ₂	CH ₂	CH ₂	CH ₃		
(Bu) ₃ P	1.53	1.2-1.4	1.2-1.4	0.9		
(Bu) ₃ P-Ni	1.84	1.5-1.7	1.5-1.7	1.02		
(Bu) ₃ P-CH ₂	2.32	1.6-1.75	1.6-1.75	1.07		
Lactone	α -CH ₂ : 2.65		β -CH ₂ : 3.40			
Polymer	+P-CH ₂ -CH ₂ -CO ₂ -(CH ₂ -CH ₂ -CO ₂) _n -CH ₂ -CH ₂ -CO ₂ ⁻					
free	2.45	2.35	4.27	2.43	4.50	3.10
complexed	broad signal between 9.7-14.7 ppm					

During the course of the polymerization and at the early stage the intensity of the signal at 1.8 ppm, corresponding to the proton in α position of the phosphorus, decreases to finally disappear at t=80 min. This disappearance is associated with a gradual fading out of the solution. At this time the comparison of the new ¹H chemical shifts values of phosphine protons with those of a phosphine sample in toluene, indicates that the phosphorus chelated nickel complex is totally destroyed (table1). Moreover no new signal may be observed in the spectrum but a very broad signal merges in from the baseline. The complex consumption varies linearly with time as shown in figure 1 (curve Z).

After a short period, about 10 min, another broad signal extending between 9.7 to 14.7 ppm appears (Figure 1). The appearance of this broad signal is concomitant to a drastic loss of resolution as observed both on the deuteriated toluene signal (Lock signal for the spectrometer) and on the ¹H resonances. The formation of this signal is associated with the consumption of phosphine (70%). Then after few minutes, new small signals at 2.32, 2.43 and 4.27 ppm appear, assignments of these signals were achieved using selective irradiations; thus the first signal (2.32 ppm) corresponds to the α -H of quaternary phosphonium while the two other signals correspond to the polymer.

Focussing on the broad signal during the course of the polymerization we could observe its continuous evolution. Indeed, the intensity of this signal decreases as the signal moves to high field and disappears when it resonates at about 4 ppm. During the polymerization both the polymer and the nickel propionate precipitate due to their poor solubility in toluene, however the

solubility of the polymer is sufficient to identify its resonances. Moreover, the solid nickel propionate does not react with the phosphine or the lactone to do again complexes.

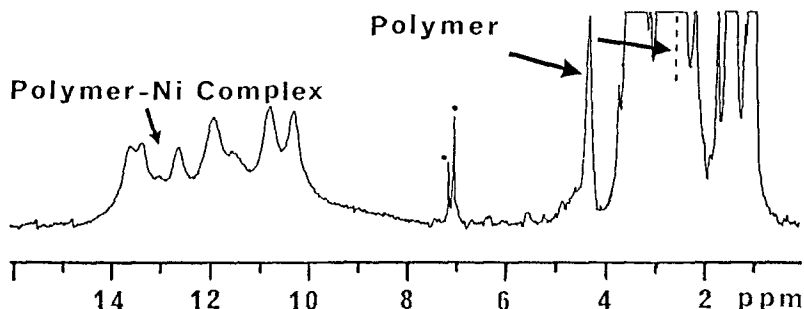


FIGURE 1: ^1H NMR spectrum of β -propiolactone polymerization. Formation of the polymer-Ni complex (●:toluene).

After 120 min the broad signal has completely disappeared and the resolution was considerably improved to a better level than at initial start of the experiment as measured on the lock signal. At this time it was interesting to notice that the solution contains a substantial amount of lactone but a small quantity of phosphine (20%) and the consumption of these compounds is achieved in a few hours. In this experiment it was difficult to localize the resonances corresponding to the first and the last terms of the polymer as they overlap with the large signals in the 2.3 to 4.3 ppm region.

Consequently we performed a second polymerization experiment leading to oligomers only (DP-4). The chemical shift values obtained are reported in table 1.

In figure 2, the curve X indicates that the dissociation of the phosphine complex is achieved in about 140 min, and as shown by curve Y, there is a stoichiometric relationship between the consumption of lactone and the dissociation of the phosphine complex. (consumption of lactone : 25%).

The formation of the broad signal corresponds to the complete consumption of the lactone. The resulting oligomers are more soluble in toluene than the polymer and we observed in this case a slight precipitation of the nickel propionate and of the oligomers. In these conditions of polymerization the broad signal observed between 9 to 14 ppm can remain for several days. Then, addition of a large excess of β -propiolactone induces its own consumption and the precipitation of both the polymer and the nickel propionate.

During the formation of the oligomer (DP-4) new signals appear in the spectrum at position 5.3, 6.1 and 6.3 ppm. These signals were not observed in the first polymerization and were assigned to acrylate chain protons ($\text{CH}_2=\text{CH}-$). These signals observed previously by Kagiya et al. (15) correspond to a chain transfer in the anionic polymerization of propiolactone.

DISCUSSION

The nickel propionate-tributylphosphine complex is soluble in toluene giving a red solution. The ^1H spectrum shows that this complex is stable in toluene over a few days, however the spectrum shows that after adding the β -propiolactone some modifications have occurred. An example of this

phenomenon is the decrease and the disappearance of the resonance at 1.84 ppm, which corresponds to the α -H of complexed phosphine. The new chemical shifts of phosphine protons and the fading out of the solution imply that the nickel phosphine complex is destroyed. Moreover the chemical shift values for these resonances agree with those corresponding to free molecules.

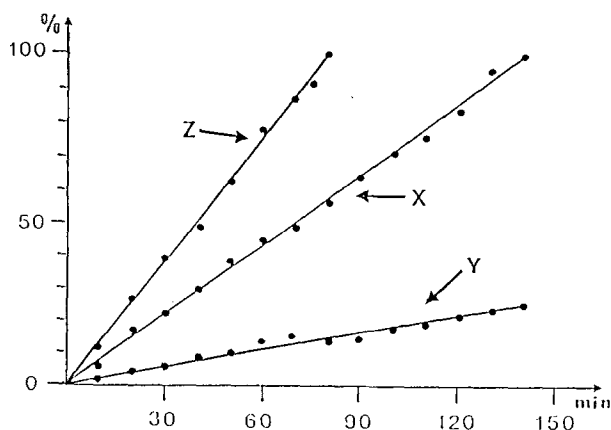
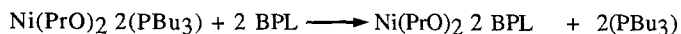


FIGURE 2: β -propiolactone and nickel propionate-tributylphosphine consumption (in%) versus time. Z: complexed phosphine for the first polymerization. X: complexed phosphine, Y: BPL for the second polymerization.

The time for the dissociation of the complex is correlated with the ratio (monomer) / (catalyst) as illustrated on figure 2 with curves X ($0.16 \text{ M.L}^{-1}/0.02 \text{ M.L}^{-1}$) and Z ($10 \text{ M.L}^{-1}/0.02 \text{ M.L}^{-1}$). At time $t=140 \text{ min}$. the consumed molecules of lactone (curve Y; 25% of 0.16 M.L^{-1}) correspond to the molecules of phosphine dissociated from the complex (curve X; 0.04 M.L^{-1}). Finally, during the dissociation of the phosphine complex the absence of $\text{Ni}(\text{PrO})_2$ precipitate which can be easily observed as this compound is not soluble in toluene, indicates that the nickel salt is involved in a new complex. According to these observations we can assume that the β -propiolactone is probably the new chelated species:



It is difficult now to say precisely which oxygen atom is responsible of the Ni-O chelate ligand, but the energies of frontier orbitals are in favour of an interaction of the nickel atom with the carbonyl group.

However other parallel reactions with consumption of free lactone should be considered too: (i) the substitution of the propionate by the dipropionate (scheme 2, A). This hypothesis implies that the carboxylate attacks the lactone, but it is in contradiction with the fact that the propionate alone initiates the polymerization slowly (12), (ii) the ring opening of the lactone by the phosphine to give a zwitterion is a second possibility, but here again in contradiction with the new chemical shifts of the phosphine. In fact the rapid dissociation of the phosphine complex is not favourable for the accomplishment of the two last reactions.

It is difficult to determine the exact nature of the observed broad signal (9.7 to 14.7 ppm) but its continuous evolution during the reaction could be

related to the concentration of the nickel salt in solution, which decreases as the polymerization progresses. Consequently this signal disappears when the nickel propionate has completely precipitated. It is interesting to note that the precipitate does not react further to give complexes showing that the nickel salt when in solid state is not reactive.

The second polymerization leading to oligomers formation, in which this broad signal can remain for several days, agrees well with the previous hypothesis. Indeed in this oligomerization we observed a slight precipitate of nickel propionate indicating that the complexed oligomer chains are soluble in toluene, and the precipitation of the nickel propionate is a consequence of the poor solubility of the polymer chains in the solvent used.

In the two experiments described in this paper, the observation of a broad signal by ^1H NMR technique might reflect an interaction between an organic compound, i.e. polymer chains and the paramagnetic nickel atom.

The appearance of new signals at 2.45 and 3.10 ppm which correspond to the consumption of phosphine, indicates that the ring opening of the complexed lactone is achieved by uncharged Lewis base and implies the formation of a zwitterion according to a mechanism proposed by Gresham et al. (16). The ring opening via a zwitterionic mechanism is reinforced by the appearance of the new signal at 2.32 ppm for the butyl group, corresponding to the α -H of a quaternary phosphonium. The fast consumption of phosphine is an other argument in favour of this mechanism, as the attack of the β - CH_2 group by the phosphine with an alkyl-oxygen cleavage ($\text{S}_{\text{N}}2$) is probably more favourable in a complexed lactone.

In anionic polymerization of β -propiolactone initiated by uncharged Lewis bases, the crucial and rate-determining step in the process of producing macrozwitterions seems to be the reaction of the betaine to the lactone (scheme 1,B) (8,9). In our polymerization scheme the reaction B is as fast as the reaction A because the consumption of phosphine corresponds to the appearance of polymer signals in few minutes (2.43 and 4.27 ppm).

The chelated Ni-BPL complexes seem to be responsible of this different behaviour. Indeed the electronic density of a complexed lactone favours the ring opening by the β -substituted carboxylate (Scheme 1-B). Moreover the consumption of only 70% of phosphine and lactone for the zwitterion formation shows that only a few complexed molecules of lactone are available to achieved the reaction B.

In the course of polymerization the consumption of lactone after the disappearance of the broad signal, indicates that the propagation step (Scheme 1, C) is achieved by the carboxylate moiety (6).

CONCLUSION

In a previous paper, the conversion versus time plots of the polymerization of β -propiolactone based on the measurements of the IR absorptions of the carbonyl groups (lactone: 1850 cm^{-1} , polymer: 1740 cm^{-1}) gave a global result of the polymerization process (12).

In the present study, a more detailed analysis of the initiation process has allowed us to show that the polymerization of the β -propiolactone initiated by the nickel propionate tri-butylphosphine catalyst system is achieved according to the following four elementary reactions.

1) The dissociation of the phosphine complex and the formation of a new complex with the nickel salt and the lactone.

2) The reaction of the "activated" lactone with the phosphine to give a zwitterion.

3) Then the reaction of the zwitterion with the complexed lactone to give in a short time a β -substituted carboxylate.

4) Finally the attack of the lactone by the carboxylate moiety to cause chain growth.

Complementary experiments, are necessary in order to be able to propose a fully comprehensive mechanism explaining the formation of the broad signal, which seems to be linked with the determining step of the polymerization process. The use of the ^{31}P NMR spectroscopy should be a good choice to confirm the formation of a zwitterion while the use of ^{13}C NMR technics would allow to follow the appearance of a broad signal, if any, during the polymerization, and also to localize the complexed oxygen atoms along the polymer chain.

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