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The role of complex formation in the anionic polymerization of L-lactide

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Summary

The rate lowering effect of crown ethers in the anionic polymerization of L-lactide is interpreted by the formation of activated monomer-cation complex. This interpretation is supported by molecular mechanics calculations. The formation of a 1:1 complex between lithium ion and L-lactide in THF was proved by ^{1}H NMR and the formation constant was measured to be 3.8 M^{-1}.

Introduction

The polymerization of L-lactide can be initiated in solution by alkali metal alkoxides. Different potassium (1,2) and lithium alkoxides (3) are frequently applied initiators. The authors reported earlier that 18-crown-6 decreases the rate of polymerization and gives rise to a polymer with narrow molecular weight distribution in the L-lactide/t-BuOK system (4). The rate lowering effect is unusual, because complexing agents convert contact ion pairs into crown ether separated ion pairs, so rather rate enhancement is expected (5,6).
In this paper we report our investigations and quantum chemical calculations on the role of L-lactide/K^+ and L-lactide/Li^+ complexes.

Experimental

The ^{1}H NMR spectra were taken on a BRUKER WP 200 SY spectrometer. LiBr (Fluka product) was dried at 150 °C overnight and dissolved in 0.1 M L-lactide solution.

Results and discussion

The rate of polymerization is much lower in the presence of crown ether with potassium counterion, but only a small extent can be spotted in the case of lithium and the complexed lithium counterion (7). Since there is no significant crown ether effect in the case of Li^+, one can not explain the rate decreasing effect by steric hindrance at the propagating chain end, i.e., the large metal ion/crown ether complex sterically hinders the reaction of the chain end.
To explain the difference between Li^+, complexed Li^+ and K^+, complexed K^+ ions molecular mechanics (force field) calculations have been carried out to estimate energy levels and to find out the effect of complexation.

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At first, we tried geometry optimization with semi-empirical quantum chemical methods (MNDO). Because of the unsatisfactory parametrization of the alkali metals, the results obtained proved to be very unreliable and contradictory in the case of three different MOPAC packages. It was not possible to decide whether a central metal complex with L-lactide is the preferred one, or an "outer" one, when the metal ion lies in the axis of the carbonyl group. This type of calculations would need complete parametrization starting from the *ab initio* level.

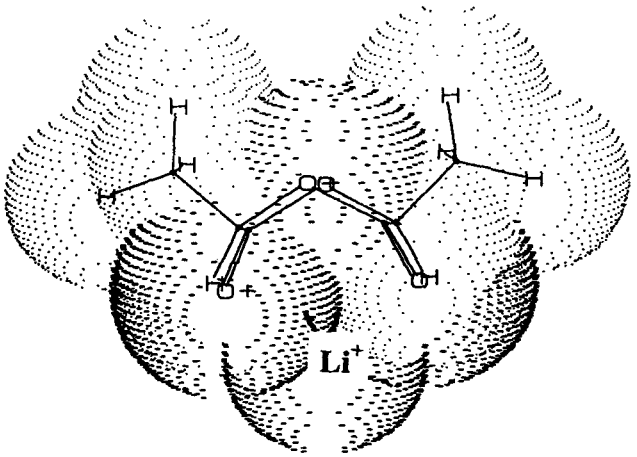

Figure 1. The "central" complex of L-lactide and Li^+ ion

Force field calculations (MM2 and MMX) yielded better results. Some modifications in the force field were performed: the ion pairs were removed from the oxygen, therefore it was necessary to alter the van der Waals parameters, as proposed in the literature (8). On the other hand, slightly modified stretching parameters were used. Making calculations from the "central" complex, the strain energy difference between the Li^+/L-lactide, Li^+/12-crown-4 complex and K^+/L-lactide and K^+/18-crown-6 complexes was calculated and found to be -75.2 kcal/mol (U_{Li} =-108.5 kcal/mol, U_K=-183.7 kcal/mol, where U is the steric energy difference between the crown ether and L-lactide complexes).

The force field calculations clearly show that the monomer may form an activated complex with the counterions and the calculated energy differences indicate that the Li^+ forms a stronger complex with the monomer than K^+ does. Thus, the K^+ complex will be destroyed by a stronger complexing agent (crown ether) but the Li^+ complex will not.

To prove the presence of the monomer/Li^+ complex, independent experiments were carried out using LiBr as a highly THF soluble salt and L-lactide. The complex formation was investigated by ^1H NMR, i.e., the extent of shifting of the characteristic quartet of CH proton in L-lactide was determined.

The typical chemical shift of CH- proton in the presence and absence of LiBr can be seen in figure 2.

The δ versus lg[LiBr] shows a definite and typical S-shape curve characteristic of a 1:1 molar ratio complex. From the Benesi-Hildebrand equation (9) we calculated the stability constant of the complex formed. This constant was found to be 3.8 M^{-1}.

Complex formation with K^+ was also proved, but due to the moderate solubility of the potassium salts the limiting value of δ and so the formation constant could not be determined.

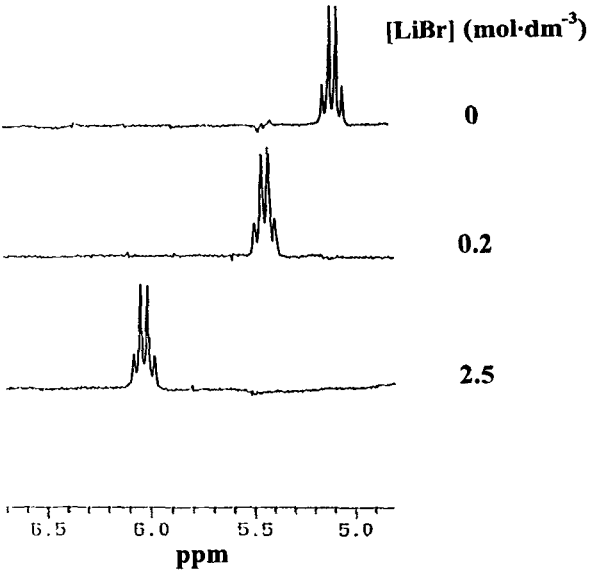

Figure 2. Dependence of the δ chemical shift of the CH resonance of L-lactide on [LiBr]. (^{1}H NMR in THF)

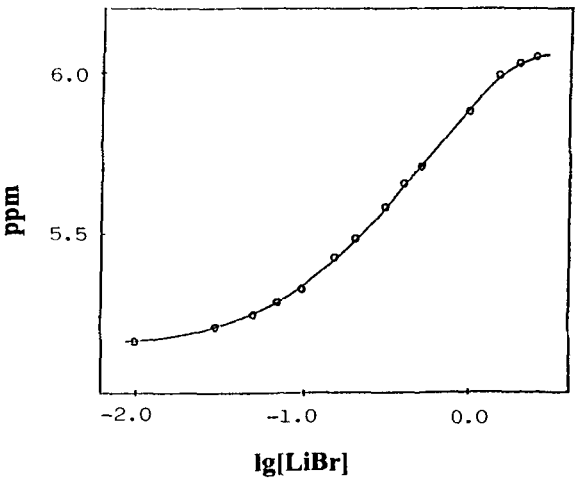

Figure 3. Dependence of the δ chemical shift of the CH resonance of L-lactide on lg[LiBr].

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