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Polymerization of Methylthiirane Initiated by Platinum(II)- and Palladium(II)-Complexes

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Summary

Some complexes derived from platinum(II) and palladium(II) initiate stereospecific polymerization of methylthiirane in homogeneous phase.

When the metal environment is chiral no stereoelective polymerization occurs. The mechanism of polymerization initiated by platinum complexes seems to be similar to those proposed for zinc or cadmium derivatives whereas analogies are apparent between palladium and some aluminum derivatives, especially in the formation of great amounts of disulfide bonds during the polymerization.

Introduction

Methylthiirane (propylene sulfide) polymerization may be initiated by many organometallic compounds derived mainly from I_A Group (1) and from II_B Group metals (zinc (2,3) or cadmium (3)). Theses polymerizations initiated by well defined organometallic compounds or salts are stereospecific only in the case of cadmium derivatives. Binary systems $ZnEt_2$: water (2) or ternary systems $AlEt_3$: water : alcohol (6) gave also stereoregular polymers.

With some chiral initiators, preferential polymerization of one of the two antipodes of methylthiirane was observed (7). These polymerizations are called stereoelective polymerizations.

Cadmium is a "soft acid" and sulfur a "soft base" in the Ahrland and Pearson classification (8) and strong interactions have been observed between methylthiirane and cadmium organocompounds (9,10). Platinum (II) and palladium(II) are also "soft acids" and complexes between these metals and cysteine or methionine have been reported (11-13). These complexes of noble metals with mercaptans and mercapto-acids are interesting because of their possible use in radiation protection, biology and medecine (14-16).

We tried to initiate methylthiirane polymerization with such complexes because platinum(II) and palladium(II) undergo large metal-sulfur interactions.

Experimental

All polymerizations were carried out in sealed apparatus using vacuum techniques. Optical activities were measured with a P. 141 Perkin-Elmer polarimeter and ^{13}NMR (25 MHz) spectra were realized with a Jeol PFT 100 (solvent CCl_4/C_6D_6 (90:10) at 60°C).

Dichloro-($\pm$methylthiirane)$_2$ platinum(II) was prepared for the first time according to the following procedure : 415 mg of K_2PtCl_4 were dissolved in 10 ml of water and added to 1.95 millimole of methylthiirane with shaking. A copious yellow precipitate was obtained and filtered. It was washed with water, with alcohol and dried at 80°C for 4 hours under vacuum. Elemental analysis : Found : C 17.2 %, H 3.1 % and S 15.4 %. Calculated : C 17.4 %, H 2.9 % and S 15.46 %.

Complexes of platinum(II) and palladium(II) with cysteine or methionine derivatives were prepared according to methods described in the literature (11-13, 17-20).

Results and Discussion

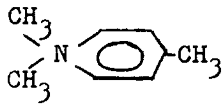
All polymerizations were carried out at 20°C without a solvent and were very slow. After several days, the initiator was soluble in the monomer (excepted for L-ethylcysteinato $Pt_{II}Cl_2$) and polymerizations took place in homogeneous phase. Solutions were always coloured from clear yellow to orange-copper. Molecular weights of polymers initiated by platinum(II) complexes are high (for example $\overline{M}_n$ = 60.000 with L-methionine $PtCl_2$ as the initiator). They are lower than 10.000 when polymerization is initiated by palladium(II) complexe.

As shown in Table 1, polymerizations initiated by platinum(IIcomplexes may be partially stereospecific. Tacticities of polymers were measured using ^{13}C NMR (21). The isotactic diad content may reach 70 %.

α-Amino acids such as methionine, cysteine and their esters were used as ligands. The derived chiral complexes of platinum(II) and palladium(II) did not lead to stereoelective polymerizations. However, we have also found that the same chiral ligands associated to cadmium initiate stereoelective polymerizations (22), and this difference should be attributed to the geometric structure of such complexes or of their aggregates. A similar situation has been described for binary or ternary systems derived from triethylaluminum which initiate stereospecific but not stereoelective polymerization of methylthiirane (6) or methyloxirane (23).

TABLE 1

Methylthiirane polymerizations initiated by platinum(II) and palladium(II) derivatives

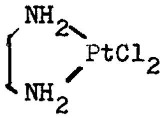
Initiator	time (months)	yield	homogeneous	contents of isotactic diads %	other observations
$\vert$L-methionine$\vert$ $PtCl_2$	2	25	+	65	*
$\vert$L-(ethyl ester methionine)$\vert$ $PtBr_2$	2,5	55	+	45	*
$\vert$L-(ethyl ester cysteine)$\vert$ $PtCl_2$	9	69	no	70	*, S-S bonds
$\vert$± methylthiirane$\vert_2$ $PtCl_2$	9	67	+	65	S-S bonds
$\vert C_2H_4\vert$  $\vert$ $PtCl_2$	8	25	+	60	
$\vert$L-methionine$\vert$ $PdCl_2$	6	45	+	-	*, 2(S-S) bonds for 3 units

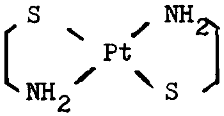
Polymerizations were run without solvent at 20°C.

* Residual monomer and polymer do not display optical activity.

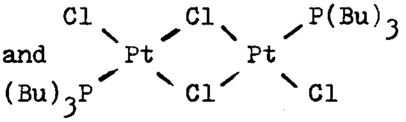
It was also observed that a polymerization initiated by the palladium(II) complex leads to a large amount of disulfide bonds in the polymer. Elemental analysis showed that we obtained 2 S-S bonds for 3 units. Such bonds were previously found in poly(methylthiirane) initiated by triisobutyl- or triethyl-aluminum derivatives (24,25). These disulfide bonds are revealed by UV spectra (24) and ^{13}C NMR (25). Some platinum(II) complexes lead also to disulfide bond formation but in small amounts.

The other following platinum(II) complexes were found to be inefficient to initiate methylthiirane polymerization :





and



Conclusion

Platinum(II) complexes slowly initiate the stereospecific polymerization of methylthiirane in homogeneous phase. Even with chiral ligands, no stereoelection was observed. The mechanism of polymerization initiated by platinum complexes seems to be similar to those proposed for zinc or cadmium derivatives.

Some analogies are apparent between the results obtained with a palladium(II) complex and with some aluminum derivatives. They both initiate methylthiirane polymerization with the formation of large amounts of disulfide bonds and these polymerizations are not stereoelective even when the metal environment was chiral. A cationic mechanism with sulfonium ions has been proposed for the disulfide bond formation during the polymerization (25) or the degradation of poly(methylthiirane) (26). A similar mechanism may be suggested for palladium(II).

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