POLYVINYLIC DERIVATIVES OF 4-ALLYLDITHIOCARBOXYLATE-5-HYDROXY-3-METHYL-1-PHENYLPYRAZOL

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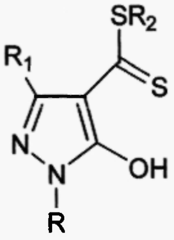
Abstract : Polymeric derivatives of 4-alkyldithiocarboxylate-5-hydroxypyrazoles have been prepared by bulk vinylic homo and copolymerization of 4-allyldithiocarboxylate-5-hydroxy-3-methyl-1-phenylpyrazol .

Introduction

The 4-alkyldithocarboxylate-5-hydroxypirazoles **I** are heterocyclic chelating ligands with interesting extractive properties, where the 5-hydroxylic and the thiocarbonyl group of the 4-dithiocarboxylate moiety are responsible for the chelation of metal ions. These ligands are prepared by condensation of 5-pyrazolones with carbon disulfide and alkyl halides, in the presence of bases like n-butyllithium, sodium acetate or quaternary ammonium hydroxides (1-4).



I

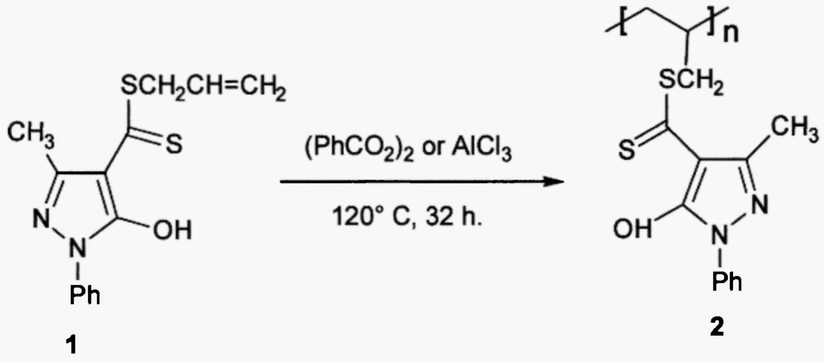
R = Alkyl, Phenyl ; R_1 = Methyl, Hydroxyl ; R_2 = Alkyl, Benzyl, Allyl

The derivatives **I** allow the solvent extraction of several divalent transition metal ions (5) and the solvent extraction separation of Cu(II) from Fe(III) in acidic lixiviation solutions of a copper mineral with a high content of iron (6). Recently, these solvent extraction studies were extended to toxic mercury, lead and cadmium elements and it was demonstrated that **I** (R = Phenyl ; R_1 = Hydroxy ; R_2 = n-Dodecyl) can be used to separate Hg(II) from Pb(II) and/or Cd(II) at pH 1, in a single extraction step (7).

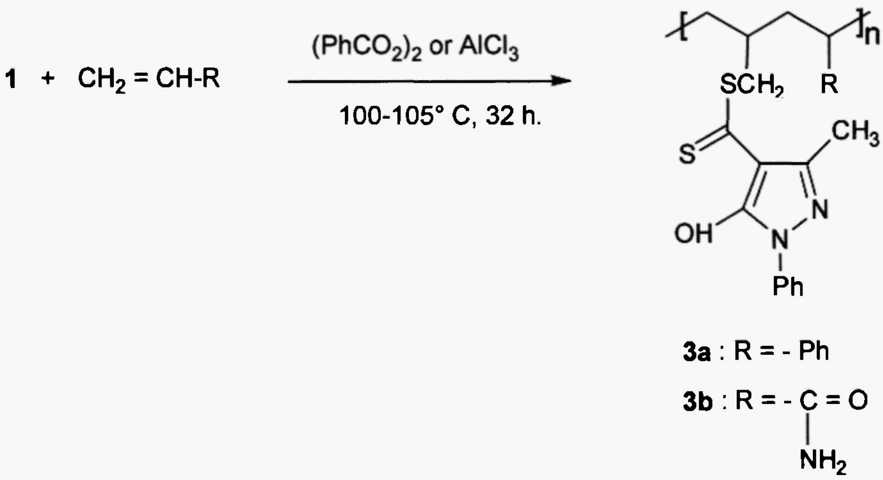
When R$_2$ in the general structure **I** is an allylic substituent it is possible to carry out vinylic polimerization and in order to get chelating polymers containing the 4-alkyldithiocarboxylate-5-hydroxypyrazol moiety, we have studied the bulk homopolymerization of 4-allyldithiocarboxylate-5-hydroxy-3-methyl-1-phenylpyrazol **1** and the copolymerization with styrene or acrylamide.

Results and Discussion

The bulk vinylic homopolymerization of **1** was performed in a opened Pyrex tube by heating 0.6007 g (2.07 mmol) of the monomer and 0.09 mmol of catalytic benzoyl peroxide or aluminum chloride in a silicon oil bath at 120° C during 32 h (8). At the end of the reaction, a flowable orange to red liquid was formed , becoming to a glasslike solid **2** at room temperature (Ec. 1). Following the same methodology, the 4-allyldithiocarboxylate **1** was bulk copolymerized with styrene or acrylamide , using a 1:1 molar ratio of the monomers. Thus, 2.07 mmol of **1**, 2.07 mmol of styrene or acrylamide and 0.09 mmol of benzoyl peroxide or aluminum chloride were heated at 100-105° C during 32 h., to afford **3a** or **3b** as a dark red likeglass solid in both cases (Ec. 2). The progress of the homo and copolymerization was analyzed by ^{1}H RMN, monitoring the dissapearance of the vinyl protons signals at 5-7 ppm or the displacement of the CH$_2$S doublet signal from 4.07 ppm in th allylic dithiocarboxylate **1** to 3.35-3.47 ppm in the polymers.



(1)



(2)

The polymers prepared were characterized by ^{1}H NMR , IR and viscosimetry. The general features in the ^{1}H NMR spectrum are a complex multiplet of the chain CH_2CH at 1.33-2.72 ppm, a slightly wide singlet of the heterocyclic CH_3 at 2.33-2.38 ppm , a difuse doublet of the CH_2S group at 3.35-3.47 ppm and a complex multiplet of the aromatic protons at 6.95-7.98 ppm (Table 1). The displacement of the CH_2S signal to higher field during the polymerization is in agreement with the chemical shift observed when this group is part of a saturated alkyl chain (3.35-3.56 ppm) (1, 4). In the IR, the polymers also display the wide and weak absorption between 3200-2700 cm-^{1}, attributed to the associated hydrogen bonding vibration of the enolic hydroxy group in the monomer (1, 9). Viscosities were measured in chloroform with a Ostwald viscosimeter at 25 ± 0.5 °C and molecular weights were estimated using the Mark-Houwink-Sakurada equation (Table 2) (10,11)

Table 1. ^{1}H NMR* data of polymers **2 - 3b** synthesized.

Polymer	-CH_2CH-	CH_3	CH_2S	Ph	NH_2
2	1.33 - 2.07	2.33	3.40	7.05 - 7.98	-
3a	1.45 - 2.08	2.35	3.35	6.95 - 7.97	-
3b	1.45 - 2.77	2.38	3.47	7.07 - 7.95	6.23

*60 MHz, $CDCl_3$, internal TMS, ppm

Table 2. Intrinsic viscosity, estimated molecular weight and glass transition temperature of polymers **2 - 3b**

Polymer	η (gdl^{-1})	Mw	Tg (°C)
2	0.808	$1.0x10^5$	91
3a	0.795	$1.7x10^5$	93
3b	0.532	$8.0x10^4$	87

Conclusions.

In conclusion, chelating vinyl polymers containing the 4-methylenedithiocarboxylate-5-hydroxy-3-methyl-1-phenylpyrazol group in the polymeric matrix have been prepared by the homo and copolymerization of 4-allyldithiocarboxylate-5-hydroxy-3-methyl-1-phenyl pyrazol. These chelating polymeric matrixes can be used in the solid-liquid separation and preconcetration of metal ions. Studies on this matter are in progress.

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