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SOLUBLE CATALYST PRECURSORS FOR DEHYDROGENATIVE POLYMERIZATION REACTION

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Two soluble catalyst precursors, Re(abt)$_3$ and Re(abt)$_2$(C$_6$H$_4$NS) can be used to generate rhenium sulfides insitu, which catalyze polyquinoline synthesis by dehydrogenative polymerization reactions. The reactive rhenium sulfides were found to have a chemical stoichiometry close to ReS$_2$.

1. Introduction

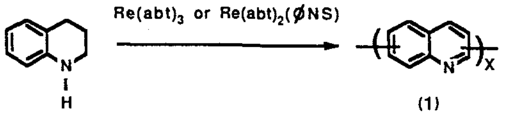
Recently we reported [1,2] that a novel catalytic dehydrogenative polymerization (CDHP) of 1,2,3,4-tetrahydroquinoline (THQ) occurs at the refluxing temperature of THQ using a solid rhenium sulfide catalyst. The reaction leads to a new synthesis of polyquinoline (PQ, *1*) and its derivatives. These materials consist of repeating quinoline units linked in a linear fashion. Structurally, they possess an extended p-electron system delocalized along the polymer chain forming a p-conduction band. They can be converted into highly conducting polymers by various chemical doping techniques [3,4] and by thermal treatment. Since unsubstituted polyquinoline (*1*) is a fully conjugated aromatic, it is generally considered to be one of the most thermally stable materials. Indeed, a high temperature (700 ° C to 1000 ° C) vapour-phase thermolysis of these PQ oligomers results in an intrinsic highly conducting polymer film [5]. No major structural disintegration of the quinoline moiety is observed below 700 ° C.

In addition to the unique properties of PQ products described above, the new dehydrogenative condensation method is attractive because: (1) the organic starting material is readily available commercially and no complicated monomer synthesis is necessary, (2) no solvent is required, and (3) the resulting polymer can only be prepared by the other methods with great difficulty. However, one drawback of this reaction is that the efficiency (yield) of polymerization and the degree of dehydrogenation in the polymeric product is highly dependent on the surface structure, chemical composition, crystallinity and surface area of the rhenium sulfide solid. Consequently, we experienced difficulty in our efforts to reproduce the yield and the form of product from batch to batch of catalyst prepared.

Here we report that this problem can be overcome by using a soluble catalyst precursor to generate active rhenium sulfides insitu as in the reaction shown in the Scheme. Several rhenium complexes were investigated and the ease of their preparation is an additional advantage. We found that tris(o-aminobenzenethiolato)rhenium complexes produced more efficient CDHP catalysts than those from tris(dialkyldithiocarbamato)rhenium complexes, although both systems generated rhenium sulfide solids with high dehydrogenation activity. It should be noted that a delicate balance between dehydrogenation and polymerization activity of catalyst is required to optimize the yield and the molecular weight of the product in the CDHP reaction.

2. Experimental

Two tris(o-aminobenzenethiolato)rhenium complexes $Re(abt)_3$ and $Re(abt)_2(C_6N_4NS)$ were used as precursors in this study. These were prepared from ammonium perrhenate and o-aminothiophenol in a solution mixture of H_2SO_4, ethanol and H_2O according to the reported procedure [6]. 1,2,3,4-tetrahydroquinoline was purchased from Aldrich and used as received.



(1)

Scheme

Procedure of the THQ Polymerization Reaction: $Re(abt)_3$ or $Re(abt)_2(C_6H_4NS)$ (3.3 g), equivalent to 3% by weight of ReS_2, was dissolved in 1,2,3,4-tetrahydroquinoline (50 ml). The mixture was allowed to react at 210 °C for 4 hrs. and then at 270 °C for 5–7 days under one atm pressure of nitrogen. After cooling to room temperature, the reaction mixture was transferred into a solution of diethylether-hexane/1 : 5 (500 ml). The resulting suspension was stirred overnight at room temperature. The insoluble solid was filtered and washed with another portion of diethylether-hexane/1 : 5 (140 ml). The mother liquor was found to contain 8% yield (4 g) of quinoline. A repeated methylene chloride extraction of the filtered solid separated the product into a methylene chloride soluble fraction and a methylene chloride insoluble fraction. The orange-brown solid obtained by evaporation of the methylene chloride soluble fraction was washed with cool-methanol (250 ml) to give brownish yellow solids of polyquinoline in 57% yield (28.6 g). The methanol washings contained orange-red semi-solids of partially hydrogenated polyquinoline in 23% yield (11.3 g). The methylene chloride insoluble fraction was further extracted with acetic acid and the insolubles treated with conc. HCl with stirring overnight. The resulting acid solution was filtered through a sintered glass frit under vacuum and neutralized by NaOH to cause the precipitation of a gray solid. The combined acetic acid and conc. HCl extracts of methylene chloride insoluble fractions gave polyquinolines in 5% yield (2.5 g). Finally, no 1,2,3,4-tetrahydroquinoline was recovered in the product.

3. Results and discussion

The TGA measurement of Re(abt)$_2$(C_6H_4NS) (fig. 1) clearly indicated a weight loss starting at 225 ° C with derivative maxima at 250 ° C, 292 ° C and 350 ° C. A 20% weight loss was reached at 500 ° C. From this data the change in chemical composition is not obvious. However, in a preliminary kinetic study we found that in the presence of 1,2,3,4-tetrahydroquinoline molecules both soluble Re(abt)$_3$ and Re(abt)$_2$(C_6H_4NS) were readily converted to finely divided hydrocarbon containing rhenium sulfide particles at 210 ° C with a weight loss of 26.9% within one hour. These kinetic data are summarized in table 1 and fig. 2. Elemental analysis reveals the formulation composition of these rhenium sulfide particles as $ReS_{2.6}C_{7.6}N_{1.1}H_{8.1}$. A sharp loss of aminobenzene and sulfur is indicated in the early stage of the reaction at 210 ° C. The composition stays relatively constant as $ReS_{2.5}C_{7.3}N_{1.1}H_{8.0}$ in the later stage at this temperature. When the temperature was raised to 270 ° C, the carbon/rhenium and sulfur/rhenium ratios were decreased further to 5.5 and 2.1, respectively, with a 33.3%

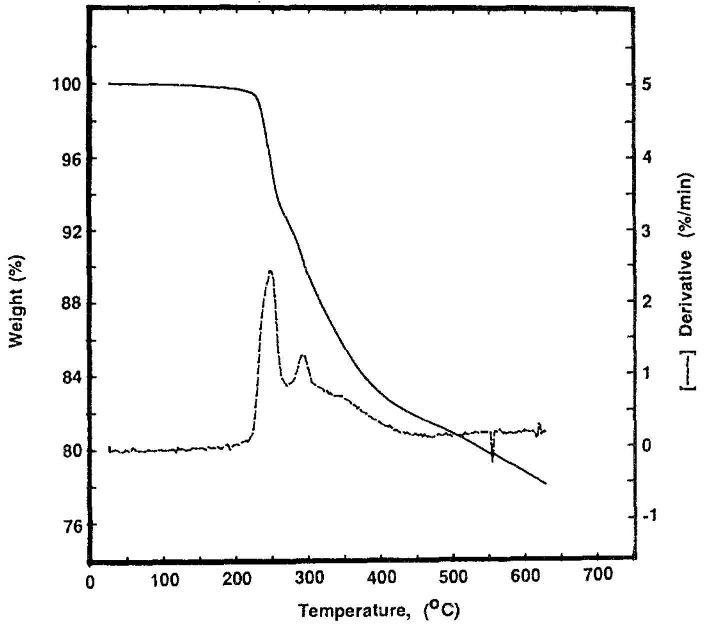


Fig. 1. The thermogravimetry analysis (TGA) of Re(abt)$_2$(C_6H_4NS) from room temperature to 650 ° C

Table 1
The time and temperature dependent thermal decomposition of $Re(abt)_3$ and $Re(abt)_2(C_6H_4NS)$

Reaction time (hr)	1	2	2.5	3	3.5	4	5	5.5	6
Reaction temperature (°C)	150	150	210	210	210	210	210	270	270
Quinoline/THQ ratio (%)	0.46	0.53	1.0	1.6	1.9	3.8	2.9	18.5	38.9
S/Re ratio	3.0	3.0	–	2.6	–	–	2.5	–	2.1
C/Re ratio	18	18	–	7.6	–	–	7.3	–	5.5
Wt. loss of $Re(abt)_3$ (%)	0	0	–	26.9	–	–	27.1	–	33.3

weight loss from $Re(abt)_3$. The composition of the latter rhenium sulfide solid was found to be $ReS_{2.1}C_{5.5}N_{0.7}H_{5.8}$. The differences between this solution thermal conversion of $Re(abt)_3$ and the solid state TGA data lead us to believe that the former process involves a reaction of the rhenium complexes with 1,2,3,4-tetrahydroquinoline. This reaction may result in the formation of quinoline and a trace amount of oligomeric materials.

Interestingly, we observed a systematic enhancement of dehydrogenative activity of rhenium sulfide solids as thermal conversion proceeded. At temperatures below 150°C, where there was no thermal decomposition of $Re(abt)_3$, the quinoline/THQ ratio of 0.46 can be essentially correlated to their thermal equilibrium constant at that temperature. This equilibrium ratio increases slightly to 1.0 at 210°C. Further increases of this ratio within a reaction period of 5 hours

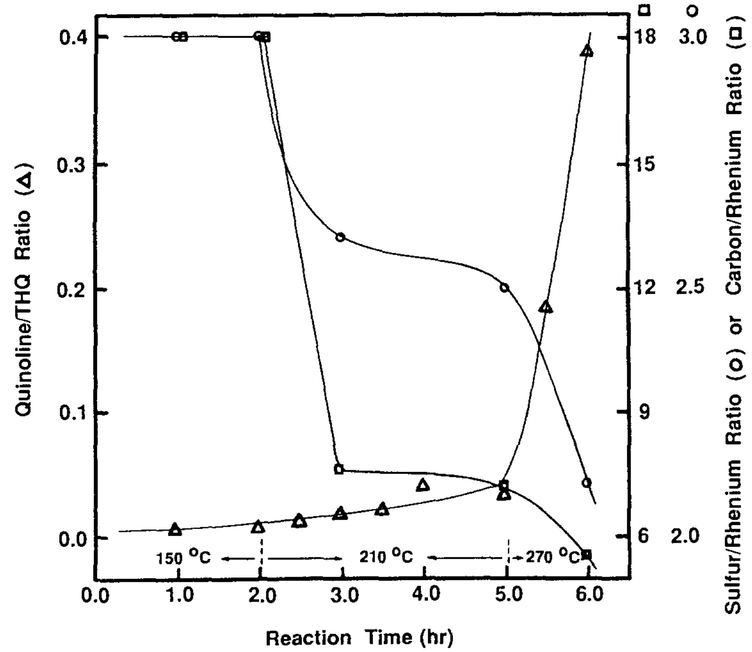


Fig. 2. The temperature and time dependent thermal conversion of $Re(abt)_3$ to rhenium sulfide solids and their dehydrogenation reactivities

Table 2
The comparison of dehydrogenative polymerization reactivity of rhenium sulfides

Method	Starting catalyst composition	% yield of QO [1] (% $CHCl_3$ insolubles)	% yield of H_xQO [2]	% yield of quinoline
1) $ReO_4^- + H_2S$	$ReS_{3.8}O_{0.6} \cdot 3H_2O$	62 (18)	33	<1
2) ReO_4^- + o-ABT [3]	$Re(abt)_3$	62 (5)	23	8
	$ReS_{2.2}$ (Alfa)	1.7 (0)	2	91

[1] Quinoline oligomer;
[2] Partially hydrogenated quinoline oligomer;
[3] o-aminobenzenethiol

indicated an onset of dehydrogenative activity of rhenium sulfide intermediates although it remained a small effect below 210 °C. Above 270 °C a very sharp rise in dehydrogenation reactivity of the catalyst was observed. It should be noted that the most reactive rhenium sulfide has a stoichiometric composition approaching ReS_2.

The spectroscopic data of the polymer fractions isolated by solvent separation bear a close resemblance to those obtained previously for the reaction of 1,2,3,4-tetrahydroquinoline over $ReS_{3.8}$ solid [1,2]. Comparison of the dehydrogenative polymerization reactivity among these two types of catalysts and a commercially (Alfa Chem.) available rhenium sulfide with a composition of $ReS_{2.2}$ is summarized in table 2. The soluble catalyst precursor, the rhenium o-aminobenzenethiolate (method 2), tends to give less of the higher molecular weight quinoline oligomers, i.e. the chloroform insolubles are formed in 5% yield compared to 18% yield obtained from the reaction with $ReS_{3.8}$ solid (method 1). Method 2 also gave a higher yield of quinoline (8%). However, the amount of partially hydrogenated quinoline oligomer fraction is decreased. These differences in the product yield reveal that the rhenium sulfides generated from rhenium o-aminobenzenethiolate have a higher overall dehydrogenation activity than rhenium sulfides used in the previous reaction [1,2].

In conclusion, we have found that the new polyquinoline structures, *1*, can be conveniently prepared by the use of soluble rhenium o-aminobenzenethiolate catalyst precursors which generate active dehydrogenation catalysts in the reaction medium. These active catalysts were found to consist of rhenium and sulfur in ratios close to ReS_2. The new method gives a reproducible synthesis of polyquinoline. It also gives products comparable to those obtained using other rhenium sulfide solids as catalysts.

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