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Nickel Catalysed Oligomerisation of Ethylene and Copolymerisation of Ethylene with Carbon Monoxide†‡

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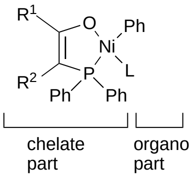
Ethylene is oligomerised and ethylene and carbon monoxide copolymerised by *in situ* nickel catalysts and aromatic sulfanyl ligands.

Polyketone, the copolymerisation product of ethylene and carbon monoxide, is of high industrial interest as the copolymer can easily be functionalised, it displays excellent physical and mechanical properties and is photodegradable. These aspects have been extensively reviewed in several papers.[2–8] The palladium catalysed synthesis, developed by Shell, reached the stage of industrial production in 1995.[9]

Nickel provides an economic alternative as it is active for oligomerisation of olefins as well as for carbonylation. The role of the chelating ligands in the olefin oligomerisation has been thoroughly investigated by Keim.[10] While the chelate part influences activity and selectivity the function of the organo part is to generate the active species and tune the selectivity.[10]

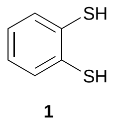


R^1 = H, Ph, SO_3Na
R^2 = OMe, Ph
L = PEt_3, PPh_3, pyridine

Fig. 1 Generalised catalyst precursor

P ^ O- and N ^ O-chelating systems turned out to produce only block copolymers in the ethylene/CO-copolymerisation.[11] *In situ* catalyst systems of Ni(cod)$_2$ and sulfanylcarboxylic acids which function as S ^ O-ligands have been patented by Keim *et al.*[12]

Here we describe the utilisation of various disulfanyl compounds in the same capacity, some of them functioning as monodentate and others as potentially bidentate ligands. The strongly chelating dithiols **1** and **2** did not catalyse the copolymerisation of ethylene/CO.



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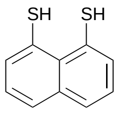

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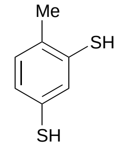
The non-chelating thiols **3–6**, in contrast, led to the formation of polyketone as well as oligomers and polymers of ethylene (Tables 1–3).

Mixtures of oligomers and polyethylene were formed with ethylene, their ratio depending on the conditions employed.



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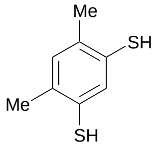

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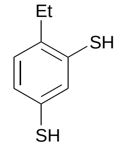

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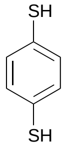

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Table 1 Oligomerisation of ethylene with Ni(cod)$_2$ and **3** or **6**

Experiment[a]	Ligand	Turnover number
1	**3**	698
2	**6**	1494

[a]Reaction conditions: 0.22 mmol ligand + 0.22 mmol Ni(cod)$_2$ in 20 ml toluene, $p_{\text{ethylene}} = 40$ bar, $T = 60$ °C, $t = 12$ h.

Table 2 Oligomerisation with Ni(cod)$_2$/**3**. Dependence of linearity and portion of 1-olefin of the C$_{10}$- and C$_{12}$-fraction on the temperature

T/°C[a]	30	60	100	140
Linearity (C$_{10}$) (%)	60.3	66.6	56.4	53.7
Portion of 1-olefin (C$_{10}$) (%)	15.9	22.2	14.4	11.9
Linearity ($_{12}$) (%)	51.6	61.1	47.4	42.4
Portion of 1-olefin (C$_{12}$) (%)	24.4	30.6	23.9	21.9

[a]Reaction conditions: 0.22 mmol **3** + 0.22 mmol Ni(cod)$_2$ in 20 ml toluene, $P_{\text{ethylene}} = 40$ bar, $T = 60$ °C, $t = 12$ h.

The homopolymer displayed a bimodal molecular weight distribution, as was confirmed by GPC analysis. GC analysis of the oligomers revealed considerable deviation from the expected Schultz–Flory distribution. This is caused by incorporation of the primarily formed products into the reaction (Fig. 2).

A perfectly alternating copolymer was obtained within a wide ethylene/CO ratio. Only traces of hexenes were obtained as by-products (Table 3). Even ligand **6**, with the sulfanyl groups in the 1,4-positions, gave considerable yields of polyketone. The material was characterised by infrared spectroscopy, melting point and elemental analysis. Infrared

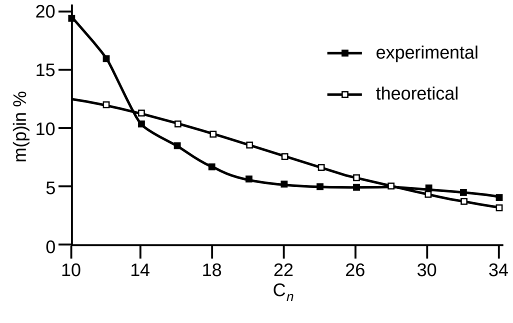

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Fig. 2 Theoretical and experimental Schultz–Flory distribution of the ethylene oligomers produced with Ni(cod)$_2$/**3**

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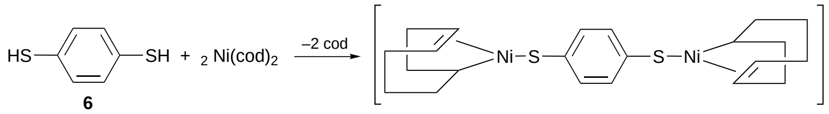
†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡Dedicated to Professor em. Dr. techn. Dipl. Ing. Dr. phil. habil. Friedrich Asinger on the occasion of his 90th birthday.



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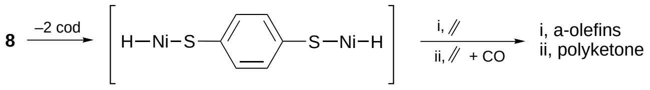

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(3)

Table 3 Ethylene/CO-copolymerisation with $Ni(cod)_2$ and non-chelating dithiols **3–6**

Experiment[a]	Ligand	Turnover number
3	**3**	287
4	**4**	165
5	**5**	149
6	**6**	113

[a]Reaction conditions: 0.22 mmol ligand + 0.22 mmol $Ni(cod)_2$ in 20 ml toluene, $p_{ethylene} = 10$ bar, $p_{CO} = 5$ bar, $T = 60$ °C, $t = 12$ h.

spectroscopy and elemental analysis showed that the polyketone was perfectly alternating.[13] According to solid state ^{13}C NMR, unbranched material was produced. Unsaturated end groups could not be detected.

Steric crowding of the phenyl ring results in lower conversions (ligands **4** and **5**). Monothiols containing electron withdrawing substituents on the phenyl ring, like 3-chlorobenzenethiol or pentafluorobenzenethiol, also showed some activity in the copolymerisation, although the rates of conversion were much smaller (turnover number 15 or 47, respectively) than with **3–6**. The reaction was unsuccessful when aliphatic dithiols like 1,2-disulfanylethane or 1,3-disulfanylpropane were used. Aromatic solvents turned out to be the most suitable (Table 4).

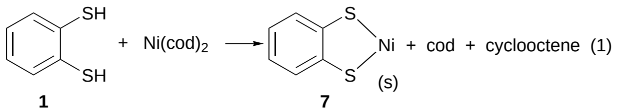
Table 4 Influence of solvent on the copolymerisation with $Ni(cod)_2$/**3**

Experiment[a]	Solvent	Turnover number
7	methanol	5
8	dichloromethane	32
9	cyclohexane	61
10	mesitylene	203
11	toluene	287

[a]Reaction conditions: 0.22 mmol $Ni(cod)_2$ + 0.22 mmol **3** in 20 ml toluene, $p_{ethylene} = 30$ bar, $p_{CO} = 10$ bar, $T = 60$ °C, $t = 12$ h.

$Ni(cod)_2$ was also replaced by other nickel salts containing a Brönsted base like acetate or acetylacetonate. The conversions were generally lower than with $Ni(cod)_2$ without change in the selectivity.

The deactivating function of ligands **1** and **2** can be explained by the formation of nickel complexes like **7** which precipitate from the solution [eqn. (1)].



(1)

1 **7**

The oxidative addition of compounds with acidic hydrogen atoms to $Ni(cod)_2$ is well known as a key step in the formation of catalyst precursors.[10] In the case of **6** this could also be observed by the disappearance of the sulfanyl resonance in the ^1H NMR spectrum. Based on this observation a hypothetical mechanism according to eqns. (2) and (3) can be proposed for the non-chelating ligands **3–6**. The mechanistic scheme accommodates the striking difference in activity between mono- and non-chelating-bisbenzenethiols by showing the formation of a binuclear hydride **9** which is not possible with monothiols.

The hydride **9** could not be detected by ^1H NMR or infrared spectroscopy. Attempts to isolate the precursor, complex **8**, or the hydride **9** from the catalyst solution were unsuccessful.

Experimental

All experiments were carried out under argon.

General Procedure for the Preparation of the Catalyst Solutions and the Copolymerisation.—The ligand and $Ni(cod)_2$ were separately dissolved at −20 °C in 10 ml of solvent. The ligand was added to the organometallic component and then the solution was allowed to warm to room temperature when it turned brown. The catalyst solution was transferred by a syringe and a Teflon cannula into an autoclave which was then pressurised with ethylene and carbon monoxide and placed in an oil bath. The turnover numbers are calculated as $mol_{products}/(mol_{catalyst} \times 12\ h)$.

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