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Polymerisation of Different Furanes with Cr(II) Surface Compounds on Silicagel

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SUMMARY

Reaction of different furanes (2,3- and 2,5-dihydrofurane, tetrahydrofurane, furane) were examined in the presence of Cr(II) surface compounds on silicagel as catalyst. In every case poly(2,3-dihydrofuran) was obtained. The products of the occuring hydrogenation, dehydrogenation and isomerisation reactions were detected by GC and NMR spectroscopy. A mechanism for the reactions is proposed.

INTRODUCTION

For saturated cyclic ethers like tetrahydrofurane (THF) the cationic ring opening polymerization to poly(oxybutylene) is well known. Conservation of ring structure was described for the cationic vinylpolymerization of 2,3-dihydrofuran (2,3-DHF) in a short communication and a patent application to poly(2,3-dihydrofurane) (poly(2,3-DHF)) (ref. 1-3).
We wish to report the formation of poly(2,3-DHF) starting either from 2,3-DHF, 2,5-DHF, THF or furane using Cr(II) surface compounds on silicagel as catalyst. Ring opening polymerization was not observed.

Cr(II) on silicagel is a highly active surface compound used for the polymerization of α-olefins (Phillips catalyst) and the elimination of oxygen impurities from gases and solvents (ref. 4-10). Due to the low coordination number of 2, stabilized by fixation to the silicagel surface, a number of π- and σ-donors bind to the Cr(II), thus constituting the first step of a catalytic reaction. Furthermore, unpopulated d-orbitals of the metal ion may act as a relay for the electron transfer between coordinated substrates.

RESULTS AND DISCUSSION

1 % Cr(II) on silicagel was prepared by a known procedure (ref. 7). For the polymerization the purified furanes were mixed with the catalyst under argon. The yields of poly(2,3-DHF) after 7 days reaction time is

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shown in table 1. The highest reactivity is observed for 2,3-DHF containing a C=C-bond for direct polymerization. The reactivity decreased from 2,3-DHF to 2,5-DHF (isomerisation to 2,3-DHF), THF (dehydrogenation to 2,3-DHF), and - drastically - to furane (loss of aromaticity and hydrogenation to 2,3-DHF) as starting monomer.

Surprisingly improved reactivity is observed using an equimolar mixture of 2,3- and 2,5-DHF. Fig. 1 shows the time dependence of polymer yield. The increase in yield indicates that the activity of the catalyst is maintained over the whole reaction time. In contrast to 2,3-DHF the 2,5-DHF and THF shows an induction period due to isomerisation or dehydrogenation to 2,3-DHF before starting the polymerization. Polymer yield increases with catalyst concentration and decreases by lowering the reaction temperatures below 273 K.

TABLE 1.

Formation of poly(2,3-DHF) starting from different furanes (reaction at 295 K for 7 days with 0.2 weight % Cr(II) corresponding to the furane)

Furane derivates	polymer yield
2,3-DHF	9.8
2,5-DHF	3.8
THF	0.9
furane	0.1

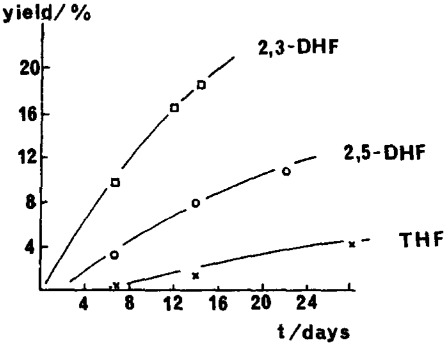
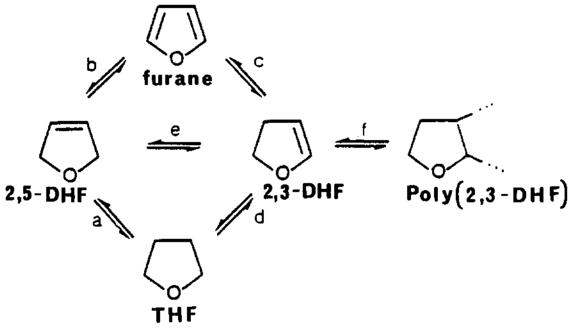


Fig. 1. Dependence of polymer yield on reaction time (reactions at 295 K with 0.2 weight % Cr(II)).

The structure of the polymers were examined by ^{1}H-NMR. The signals at σ 1.8 and 3.8 ppm (ratio 1:1) are different from the signals of polyoxybutylene at σ 1.65 and 3.45 ppm.

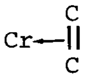
As mentioned before all cyclic ethers gave poly(2,3-DHF) in the presence of the catalyst. To detect some low molecular intermediates the solutions were examined directly by gas chromatography. Starting from 2,3-DHF the following compounds were found beside the polymer (s. table 1) after a reaction time of 7 d at 295 K: 2,5-DHF (9 %), THF (3 %), furane (4 %). THF gave 2,3-DHF (1 %), 2,5-DHF (1 %), furane (5 %). Also from 2,5-DHF and furane the other cyclic ethers were obtained. According to these results the following reaction scheme is proposed.

a-d: hydrogenation, dehydrogenation reactions;
e: isomerisation reaction;
f: polymerization reaction.



Preliminary reaction mechanisms are proposed for the hydrogenation/dehydrogenation and polymerization steps based on the following arguments:

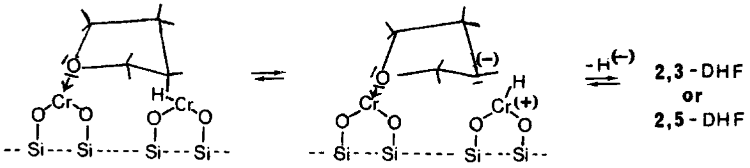
- The Cr(II)-catalyst is not consumed.
- To explain the long time activity, all bonds at the surface and thus all reaction steps (possibly excluding the polymerization) must be reversible.
- With all monomers, including the dihydrofuranes coordination via the electron donating oxygen atom will be much favoured. Thus conversion at the other reaction centers is severely obstructed.
- For the polymerization a coordinative cationic mechanism is most probable. A homopolar mechanism is ruled out as the strong Cr←C bond will obstruct the

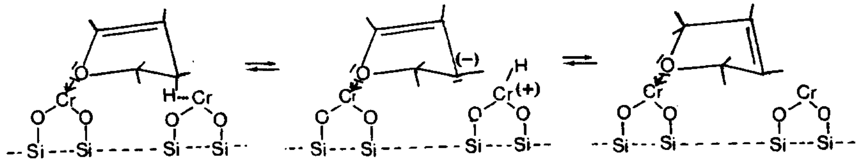


$$\mathrm{Cr}\leftarrow\begin{array}{c}\mathrm{C}\\ \|\\ \mathrm{C}\end{array}$$

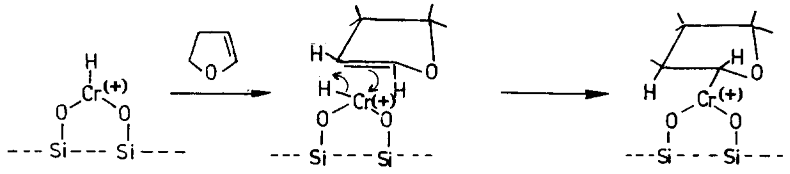
interaction, and because of the general preference of vinylethers for cationic polymerization.
- Starting from 2,3- or 2,5-DHF no hydrogen gas was detected. Formation of furane was only marginally higher than that of THF. So the balance of hydrogen might be consumed by cationic polymerization mechanism. Starting from THF only small amounts of hydrogen were found. It is mainly consumed by starting the polymerization reaction and perhaps by reduction of small amounts of Cr(III) present on the surface.

In the first step, interaction of furanes like THF or 2,3-DHF with the metal ions on surface leads to coordination of the oxygen atom followed by H^+ abstraction to the neighbouring Cr(II) (for Cr(II) pairs see ref. 8 and 11) forming a hydrogenated Cr(II) (for H-Cr(II) see ref. 10). Note that the distance between the two Cr(II) centers of the pair and the oxygen of β-position of the furanes is nearly the same: ~3 Å. Stabilization will lead to 2,3- or 2,5-DHF (from THF) and 2,5-DHF (from 2,3-DHF).

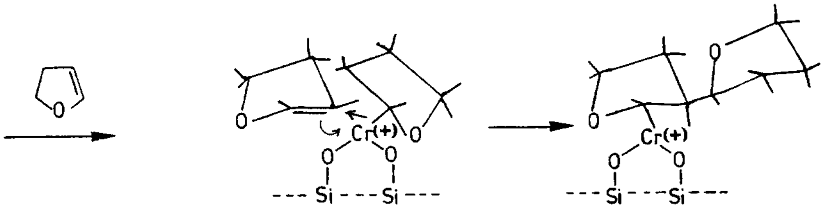




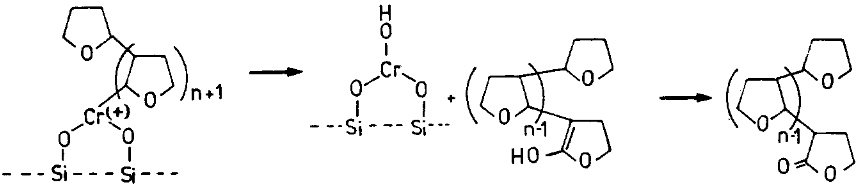
Postulating these reversibly formed hydrogenated Cr(II) centers the polymerization mechanism is formulated as follows:
- interaction of a hydrogenated Cr(II) with a C=C-bond to form a transition metal-carbon bond.



- Insertion of another monomer into the Cr-C bond under chain growth.



- Chain termination by admission of air and/or water oxidation of Cr(II) to Cr(III) and, for example, formation of carbonyl end groups (IR: 1760, 1720 cm^{-1}).



EXPERIMENTAL

Argon was dried over molecular sieve (3Å) and residual oxygen was removed by a Cr(II)/silicagel column. The furanes were purified by known procedures to remove water and destilled under argon. The purity was controlled by ^1H-NMR and GC. All reactions were carried out under purified argon.

The Cr(II) doped silicagel was prepared after a known procedure (ref. 7) under the following conditions: silicagel "Merck 7733"; activation at 500°C and reduction with CO at 500°C; Chromium concentration about 1 % on silicagel.

General description of polymerization:
10 g catalyst and 50 g monomer (2,3-DHF; 2,5-DHF; THF or furane) were mixed in a Schlenk vessel (weight ratio of monomer: Cr(II) = 0.2 %). After closing the vessel the reaction was carried out at different reaction times and temperatures without stirring and shaking. After opening the vessel to air the colour of the catalyst changed from blue violett to green (Cr(II) to Cr(III).

A small amount of the solution was directly examined by GC (sebacic acid on kieselguhr at 70°C, FID) using the different furanes as standards. Exemplary the fraction were detected by GC/MS.

For isolation of the polymer the mixture of solution and catalyst was filtered in a soxhlet apparatus through a sleeve. The catalyst residue was directly extracted with the solution for 2 hours.
Afterwards the low molecular compounds were removed in vacuo.

The viscous residue was handled in a bulb tube at 120°C to remove oligomeric compounds. The polymer obtained is a highly viscous liquid partly getting cristallin.

IR (film) : 3420 (m; OH); 2940, 2870 (s; CH); 1760, 1720 (n,w; C=O); 1360, 1340 (w; OH); 1170, 1030 (s; C-O-C) cm^{-1}
^1H-NMR ($CDCl_3$): δ= 1.8 (s; $H^{3,4}$); 3,8 (s; $H^{2,5}$); 5 (s, OH). Intensity ration 1:1: very low.

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