JOURNAL OF CATALYSIS 88, 424–430 (1984)

Surface Compounds of Transition Metals

XXVIII. Polymerization of *n*-1-Alkenes with Surface Chromium(II) on Silica Gel Support at Low Temperatures and Normal Pressure[1,2]

KARIN WEISS AND HANS-LUDWIG KRAUSS

Laboratorium für Anorganische Chemie, Universität Bayreuth, Universitätsstrasse 30, D 8580 Bayreuth, Federal Republic of Germany

Received April 21, 1983; revised February 24, 1984

By reaction of linear 1-alkenes (C_nH_{2n} with $n = 3, 4, 5, 6, 7, 8$, and 12) with surface chromium(II) at temperatures ≤20°C and atmospheric pressure, poly-1-alkenes are formed in good yields. Ethylene produces a small amount of products only. The conversion rate depends on the concentration of the monomer, on the concentration of Cr(II) in the catalyst and on the quality of the catalytic sites. The molecular weight, typically in the range of 10^4 with a broad distribution, increases with lower reaction temperature. After the polymerization, the reaction product may be isolated by extraction and a new run can be performed with the same catalyst and the same or another monomer. Mixtures of two different linear 1-alkenes obviously undergo copolymerization since the corresponding mixed oligomers can be found.

INTRODUCTION

The "Phillips catalyst" (surface chromium(VI) on silica gel or SiO_2/Al_2O_3 support) is used worldwide as a catalyst for the polymerization of ethylene at medium pressures and temperatures around 100°C (*1*). Its activity for the polymerization of higher 1-alkenes is also known (*2*), again using elevated temperatures and elevated pressures. Reduced Phillips catalysts (surface chromium(II) on silica gel support) were found to polymerize, besides ethylene, the 1-alkenes C_3H_6 and C_4H_8 to a limited extent (*3*). Under the experimental conditions of higher temperatures/higher pressures propene and 1-butene form products of low molecular weight predominantly.

In attempts to synthesize cyclopropanes from diazo compounds and olefins with surface chromium(II) catalysts (*4*), unexpectedly the polymers of the 1-alkenes used were found to be formed already at 0°C and atmospheric pressure. Obviously the catalysts were active for the polymerization of higher olefins under very mild conditions. This seems to be interesting since side reactions such as chain degradation, isomerization, and alkane formation (*5*), which play an unfavorable role at higher temperatures, can be neglected under these conditions: the chain propagation proceeds undisturbed and the catalyst undergoes no deactivation.

EXPERIMENTAL

All experiments were carried out under argon; oxygen and other impurities were removed by surface chromium(II)/silica gel (*6*).

Propene and 1-butene were purified by surface manganese(II)/silica gel (*7*). The other olefins (Fluka) were purified by Al_2O_3-N-Super (Wölm) or distillation under argon.

Surface chromium on silica gel support was prepared according to Ref. (*8*).

The following instruments were used for

---

[1] Part XXVII: Morys, P., Goerges, U., and Krauss, H. L., *Z. Naturforsch. B* 39, 458 (1984).

[2] Corresponding to Part V in the series: "Investigations of Polymerizations and Metathesis Reactions"; Part IV: K. Weiss *in* Studies in Surface Science and Catalysis, Elsevier Publishers, Amsterdam, 1984.

0021-9517/84 $3.00

analytical measurements: (i) Gas chromatography: Carlo Erba Fraktocap 2150 with FID; capillary column 30 m OV 101; Spectra Physics Minigrator; (ii) GC/MS: Varian MAT 312 (70 eV); 25-m capillary column OV 101; (iii) Gel permeation chromatography: (a) HPLC Waters ALC 200 with column PlGel (Polymer Laboratory) for low molecular weight, column 10^4-nm Styragel for high molecular weight; solvent tetrahydrofurane; polystyrene calibration; (b) GPC 200 (Waters Associates) with four Styragel columns (10^5, 10^4, 10^3, and 10^2 nm); solvent 1,2,4-trichlorobenzene; polyethylene calibration; (iv) ^{13}C NMR: Jeol FX 90 Q (solvent $CDCl_3$; internal TMS); (v) ir: Beckman 4240 (film spectra).

The reaction of olefins with chromium(II) catalysts were carried out according to method (a) for gaseous olefins, and method (b) for liquid olefins. The course of the reactions was followed by taking 2-μl samples at appropriate intervals and measuring the amount of monomer still present (GC).

(*a*) *Preparation of Polypropylene*

A suspension of 3.7 g catalyst (surface chromium(II) 800/350[3] (*8*) with 0.94% Cr(II), corresponding to 0.67 mmol Cr) in 100 ml pentane was cooled to −60°C. Propene (4.9 g) (117 mmol) was added by condensation. The color of the catalyst changed from dark green to dark blue. The mixture was allowed to warm up to room temperature within 2 h (argon-filled safety valve!). After 15 h the liquid was poured off and the catalyst was washed three times with 30 ml pentane each. After evaporation of the solvent *in vacuo*, 1.76 g of opaque colorless polypropylene were collected, corresponding to a yield of 36%.

The remaining catalyst was suspended again in 100 ml pentane, cooled to −60°C and reacted with another amount of propene (3.52 g corresponding to 84 mmol) as before. In the second run 1.2 g polypropylene was formed, corresponding to a yield of 34%. The total crop of polypropylene was equivalent to 104.5 mol propene/mol Cr(II).

Infrared spectra of the products showed absorptions at 968 and 1150 cm^{-1} which are characteristic of atactic polypropylene (*9*). No oligomers (C_nH_{2n} with $n < 30$) were found by GC in the reaction mixture.

(*b*) *Preparation of Poly-1-octene*

Surface chromium(II) (800/350) (6.6 g with 0.94% Cr(II), corresponding to 1.2 mmol Cr) was suspended in 100 ml pentane at room temperature. 1-Octene (15 ml) (96 mmol) was added; the color of the catalyst turned from dark green to bluish green. The mixture was shaken for 20 h; then the solution was separated, the catalyst extracted three times with 30 ml pentane each and the solvent evaporated *in vacuo* from the combined solutions. Polyoctene was isolated as a colorless, viscous, and adhesive residue in a yield of 10.2 g corresponding to 95%.

To the extracted catalyst, suspended in 100 ml pentane, again 1-octene (15 ml) was added. The yield of the second reaction was 10.7 g polyoctene corresponding to 100%.

A third reaction of 15 ml 1-octene with the same catalyst yielded again 10.7 g polyoctene corresponding to 100% of the 1-octene used. In total, 237 mol 1-octene/mol Cr(II) was converted.

The samples of the first and the third runs were characterized by gel permeation chromatography and found to be identical. Traces of oligomeric octenes (C_nH_{2n} with $n = 16, 24$) were found by gas chromatography in the pentane solutions.

The experimental conditions for the preparation of the different poly-1-alkenes are given in Table 1 together with a characterization of the products by ir and ^{13}C NMR.

Typical experiments were duplicated with a nonreduced Phillips catalyst (surface chromium(VI)) and with a chromium-free "equally treated" (*10*) support under the same conditions.

---

[3] First number: temperature of activation in oxygen (°C); second number: temperature of reduction in CO (°C).

TABLE 1

Experimental Conditions for the Preparation of Poly-1-alkenes and Characterization of the Reaction Products by ir and ^{13}C NMR

Monomer	Catalyst[a]	Type (a,b)[b] and temperature of reaction	Yield of poly-1-alkenes based on monomer conversion after ~20 h (%)	ir absorption $[cm^{-1}]$		^{13}C NMR: δ in ppm, internal TMS in $CDCl_3$		
Propene 4.9 g = 117 mmol	(800/350) 0.94% Cr(II) 3.7 g ≙ 0.67 mmol	(a) −60 to +20°C	37	968 1150 1385 1465	2850 2880 2930 2980	14.6[c] 17.0[c] 19.7 20.7 21.6 27.8	30.4 34.6[c] 45.6 46.1	
1-Butene 6.4 g = 114 mmol	(800/350) 0.96% Cr(II) 16.3 g ≙ 3.0 mmol	(a) −60 to +20°C	69	765 1370 1380 1445 1465	2860 2880 2930 2980	10.67 12.86 23.28 26.20 26.51 27.13	30.15 33.57 33.98 34.97 36.69	38.62 39.23 42.11
1-Pentene 6.4 g = 91 mmol	(800/350) 0.96% Cr(II) 13 g ≙ 2.4 mmol	(b) 20°C	99	730 910 1380 1460 1465	2860 2870 2930 2980	14.66 19.61 21.33 32.47	33.35 36.63 37.43 40.44	
1-Pentene 6.4 g = 91 mmol	(800) 0.5% Cr(VI) 13 g ≙ 1.3 mmol	(b) 20°C	2	720 735 880 970 1380 1460	1470 1645 2860 2880 2930 2970			
1-Hexene 10 g = 120 mmol	(800/350) 0.94% Cr(II) 5.3 g ≙ 0.96 mmol	(b) 20°C	80	720 1380 1460 1470	2870 2880 2935 2965	13.95 22.99 28.51 30.30	32.20 33.61 40.22	
1-Hexene 6.7 g = 80 mmol	(800) 0.5% Cr(VI) 33 g ≙ 3.1 mmol	(b) 20°C	38	725 965 1380 1460 1470	2860 2880 2930 2960	14.18 22.76 23.28 28.78 32.03	32.52 40.30	
1-Hexene	"Equally treated support" (10)	(b) 20°C	No reaction					
1-Heptene 10.4 g = 106 mmol	(800/350) 1% Cr(II) 16 g ≙ 3.1 mmol	(b) 20°C	70	720 1380 1460 1470	2860 2880 2930 2960	14.16 22.82 26.57 28.33 30.02	32.10 32.57 34.35 40.35	
1-Octene 17.9 g = 160 mmol	(800/350) 0.96% Cr(II) 12.5 g = 2.3 mmol	(b) 20°C	99	720 1378 1459 1466	2860 2880 2930 2970	14.14 22.80 26.55 28.00 29.14	29.99 32.07 34.18 35.00 40.55	
1-Octene 17.9 g = 160 mmol	(500/500) 0.77% Cr(II) 12.3 g ≙ 1.8 mmol	(b) 20°C	96	720 1380 1420 1460	1645 2860 2880 2930 2965	14.08 22.80 26.53 30.01 32.06	32.65 35.00	
1-Octene 17.9 g = 160 mmol	(800) 0.5% Cr(VI) 12.8 g ≙ 1.2 mmol	(b) 20°C	8	725 890 970 1380 1460 1470	1650 2860 2880 2930 2970	14.00 22.80 29.37 29.98 32.06	36.19 108.40 130.40	
1-Octene	"Equally treated support" (10)	(b) 20°C	No reaction					
1-Dodecene 11.4 g = 68 mmol	(800/350) 0.94% Cr(II) 8.5 g ≙ 1.5 mmol	(b) 20°C	99	720 1380 1455	1470 2830 2930 2960	14.02 22.72 29.49	29.81 29.92 32.03	

---

[a] First number in parentheses: temperature of activation in oxygen (°C), second number: temperature of reduction in carbon monoxide (°C).

[b] See Experimental section.

[c] Signals due to $-(CH_2)_nCH_3$ branching of the chain, $n \neq 0$.

RESULTS AND DISCUSSION

In the present work we report the polymerization of linear 1-alkenes (C_3 to C_8 and C_{12}) by reaction with reduced Phillips catalyst at temperatures from −60°C (propene and 1-butene) to room temperature (all other olefins).[4]

The separation of reaction products was usually carried out after a polymerization time of ~20 h by extraction with pentane. The resulting polymers, whose molecular structure may look like twisted carpet fringes, exhibit remarkable physical properties. Some members are very good lubricants and at the same time are strongly adhesive (C_5–C_8 polymers). In spite of their high molecular weights they all are well soluble in nonpolar solvents; this property offers considerable advantages for physical examinations and chemical applications. The polymers are from glass-like to opaque solids (polypropene, polybutene, and polypentene) or viscous oils and contain only traces of oligomeric olefins. Ethylene, in contrast, forms a small fraction of low-molecular-weight material when reacted under the same conditions as propene. (Some polyethylene of high molecular weight could have escaped isolation because of its insolubility.)

The yields of the polymerization under standard conditions (not optimized) are given in Table 1.

We found the yield of parallel reactions using a surface chromium(VI) catalyst to be remarkably lower. Since this chromium species undergoes reduction by olefins (*11*), the reduced form of the metal may be considered as the necessary constituent of the active centers (*12*). Incomplete reduction of the Cr(VI) under our reaction conditions (low temperature) and consequently a modest concentration of catalytic sites will then cause minor yields; in addition, organic oxidation products (*13, 14*) could poison active sites by chemisorption. (Use of higher temperatures may overcome both these effects but simultaneously leads to unwelcome side reactions, e.g., shift of the double bond (*5*).)

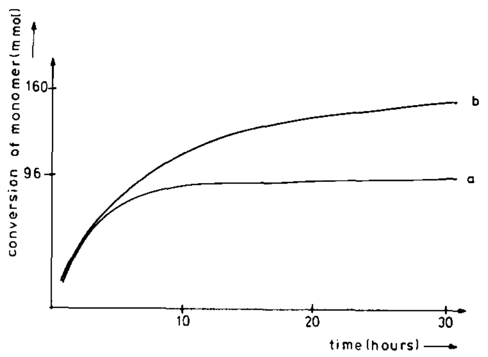

FIG. 1. Polymerization of 1-octene at different monomer concentrations. Catalyst: surface chromium(II) with 1.0% Cr(II) content. (a) 2.2 mmol Cr(II) + 96 mmol 1-octene in 100 ml pentane, 20°C; (b) 2.3 mmol Cr(II) + 160 mmol 1-octene in 100 ml pentane, 20°C.

The chromium-free "equally treated" silica gel (*10*) does not polymerize 1-alkenes (1-hexene, 1-octene).

With high monomer/chromium ratios (as in the first hours of our experiments) the rate of conversion seems to be limited by the turnover at the individual catalytic centers: there is practically no dependence on the monomer concentration during the first hours of the reaction (Fig. 1). Therefore, full conversion is reached earlier in a run with lower monomer concentration c_0. With decreasing monomer/chromium ratio during the process the reaction seems to become more and more diffusion controlled; in addition the increasing viscosity of the solution will slow down the rate further (Fig. 1, high concentration run).

At constant monomer concentration c_0 the rate of conversion increases with increasing Cr(II) content of the catalyst—with 800/300 samples up to values of ~2% Cr(II).

Finally, the polymerization rate turns out to be dependent on the thermal pretreatment of the catalyst ("quality" (*8*)). If in-

---

[4] The corresponding reaction of branched alkenes and of alkenes with the double bond in other than the 1-position will be presented in a following paper.

TABLE 2

Average Molecular Weights ($\bar{M}_w$) of the Poly-1-alkenes (Gel Permeation Chromatography)

Polymer	Temperature of polymerization [°C]	$\bar{M}_w \times 10^{-4}$[a] Solvent: tetrahydrofurane Polystyrene calibration (PS)	$\bar{M}_w \times 10^{-4}$[b] Solvent: 1,2,4 trichlorobenzene Polyethylene calibration (PE)
Poly-1-propene	−60 to +20	5.6; 2.0	2.6
Poly-1-butene	−60 to +20		2.6
Poly-1-pentene	20		2.3
Poly-1-hexene	20	5.6; 2.6	2.8
Poly-1-heptene	20		3.7
Poly-1-octene	20	5.6; 2.3	3.2

[a] Two maxima.

[b] The resolution of these measurements was not sufficient to separate two maxima.

stead of the standard catalyst 800/350 a surface chromium(II) of the type 500/500 is used, the rate of conversion is considerably lower; in addition the amount of oligomers—e.g., $C_{16}H_{32}$ and $C_{24}H_{48}$ from 1-C_8H_{16} (each as mixtures of isomers), characterized by GC/MS—was nearly doubled as compared to the same experiment with the standard catalyst. These results suggest that here the chain propagation is terminated at early stages more frequently, probably due to a competing isomerization reaction. Alkenes with the double bond not in the 1-position undergo no polymerization with surface chromium(II) catalysts under our experimental conditions.

The molecular weight distribution of the polymers produced by surface chromium(II) catalysts was characterized in different cases by gel permeation chromatography (Table 2). Polystyrene (PS) and polyethylene (PE) were used as standards for calibration; therefore the values of molecular weight give a rough estimate only. Surprisingly the data are almost independent of the monomer used; this phenomenon is not yet understood. In the molecular weight distributions of polypropene, poly-1-pentene, and poly-1-octene (Fig. 2), two maxima can be separated (PS); the oligomeric fraction of the products is very small.

With ethylene, in contrast, oligomers are the only product isolated (in very low yields). By GC/MS it was shown that they all have the formula $(C_2H_4)_m$; cleavage of the double bond and transfer of CH_2-units can therefore be excluded under our conditions. Beside the oligomeric 1-alkenes lower amounts of two other isomers are formed.

With surface chromium(VI) as a catalyst, the polymer (e.g., polyoctene) shows a drastically different molecular weight distribution, namely extremely broad without a significant maximum, and with a rather large fraction of low-molecular-weight products (Fig. 2d).

The molecular weight distribution is not only dependent on the oxidation number of

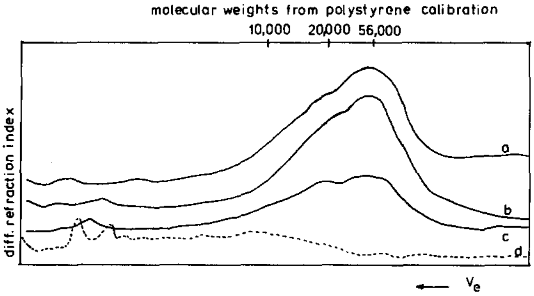

FIG. 2. Molecular weight distribution of poly-1-alkenes. The molecular weights were determined by gel permeation chromatography; the elution volumes were calibrated with polystyrene (PS) samples of known molecular weight. A differential refractometer was used as detector. (a) Poly-1-octene (20°C, Cr(II) catalyst), (b) poly-1-hexene (20°C, Cr(II) catalyst), (c) polypropene (−50 to +20°C, Cr(II) catalyst), (d) poly-1-octene (20°C, Cr(VI) catalyst).

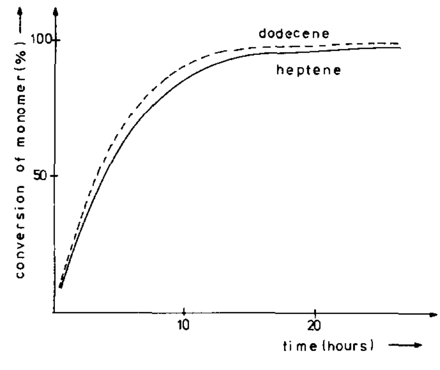

FIG. 3. Copolymerization of 1-heptene and 1-dodecene: Conversion of monomers in percentage. Surface chromium(II) catalyst with 1.0% Cr(II). Reaction of 8.5 mmol Cr(II) with a mixture of 63 mmol 1-heptene and 45 mmol 1-dodecene in 100 ml pentane at 20°C.

the chromium, but turns out to be a function of the temperature of polymerization as well. As reported in Ref. (*2*) the average molecular weight of polyethylene formed by catalysis with surface chromium(VI) increases with decreasing reaction temperature. Also in our experiments (polymerization of 1-pentane and 1-octene with surface chromium(II) catalyst) a lowering of the reaction temperature from +25 to −30°C results in a significant increase of the molecular weight up to 10^5–10^6 (PS) with a very broad molecular weight distribution and a remarkable fraction of oligomers. On the other hand, as was shown recently (*15*), the reaction of 1-octene with surface chromium(II) without solvent under reflux (bath temperature 175°C) produces polymers with very low molecular weight (PS).

In a standard polymerization procedure as described above (1-alkenes/surface chromium(II) on silica gel/room temperature or lower/inert solvent) the catalysts remain active after the extraction of the polymer with pentane (not with ether!); they may be used for another polymerization of the same or another monomer. For example, after reaction with 1-butene and extraction of the polybutene with pentane a surface chromium(II) catalyst polymerizes 1-octene to polyoctene quantitatively. After three runs with 1-octene the polymers isolated from the pentane extractions show the same molecular weight distribution for the first and the last run. After the polymerization reaction and extraction with inert solvent the active sites obviously remain "alive."

The active sites do not distinguish between different 1-olefins. Simultaneous polymerization of (a) 1-heptene and 1-octene or (b) 1-heptene and 1-dodecene with a surface chromium(II) catalyst show nearly the same time/conversion dependence for the pair of alkenes used (see Fig. 3 for (b)). By GC/MS analysis of the small oligomeric fraction formed together with the polymers we found that the low-molecular-weight products contain oligomers consisting of one olefin as well as "mixed" oligomers (Table 3). Thus, if oligomers and polymers are formed according to the same reaction mechanism, we may conclude that a real copolymerization occurs.

On the basis of the present results it would be too early to propose a reaction mechanism, keeping in mind that there is still no generally accepted explanation of the Phillips polymerization of ethylene itself, both with Cr(VI) and Cr($<$VI) cata-

TABLE 3

GC–MS Identification of Oligomeric By-products from a Copolymerization of 1-Heptene/1-octene and 1-Heptene/1-dodecene

1-Heptene/1-octene
M^+ = 196 (heptene)$_2$]$^+$
M^+ = 210 (heptene–octene]$^+$
M^+ = 224 (octene)$_2$]$^+$
M^+ = 294 (heptene)$_3$]$^+$
M^+ = 308 (heptene)$_2$ octene]$^+$
M^+ = 322 (heptene) (octene)$_2$]$^+$
M^+ = 336 (octene)$_3$]$^+$

1-Heptene/1-dodecene
M^+ = 196 (heptene)$_2$]$^+$
M^+ = 266 (heptene–dodecene]$^+$
M^+ = 336 (dodecene)$_2$]$^+$

Catalyst: surface chromium(II) on silica gel support (800/350 with ~1% Cr(II)).

lysts. Nevertheless, some remarks on the chemistry of our reaction can be made:

(i) Cr(VI) catalysts are less effective than the corresponding Cr(II) products under our temperature conditions. This suggests that a low oxidation number of the metal is important.

(ii) Catalysts with highly unsaturated chromium centers are the most active ones. This points to an important role of complex formation as an initial step.

(iii) An at least bimodal molecular weight distribution of the polymers is found. This may be due to the occurrence of more than one reaction and/or mechanism.

ACKNOWLEDGMENTS

The authors are grateful to Professor H. Hoecker for discussion, to Miss Petra Kindl for preparative work, and to Dr. G. Gann, Farbwerke Hoechst, for determinations of molecular weights (PE). They also thank the Fond der Chemischen Industrie and the Farbwerke Hoechst AG for financial support.

REFERENCES

1. U.S. Pat. 2825721 and 2960126 (1958).
2. Clark, A., Hogan, J. P., Banks, R. L., and Lanning, W. C., *Ind. Eng. Chem.* **48,** 1152 (1956).
3. Krauss, H. L., and Stach, H., *Z. Anorg. Allg. Chem.* **366,** 280 (1969).
4. Weiss, K., and Hoffmann, K., *J. Mol. Catal.*, in press.
5. Krauss, H. L., and Hums, E., *Z. Naturforsch. B* **34,** 1628 (1979).
6. Moeseler, R., Horvath, B., Lindenau, D., Horvath, E. G., and Krauss, H. L., *Z. Naturforsch. B* **31,** 892 (1976).
7. Horvath, B., Moeseler, R., Horvath, E. G., and Krauss, H. L., *Z. Anorg. Allg. Chem.* **418,** 1 (1975).
8. Krauss, H. L., Rebenstorf, B., and Westphal, U., *Z. Anorg. Allg. Chem.* **414,** 97 (1975).
9. Hummel, D. O., and Scholl, F., "Atlas der Polymer- und Kunststoff analyse," Vol. 1. Verlag Chemie, Weinheim, 1978.
10. Hierl, G., and Krauss, H. L., *Z. Anorg. Allg. Chem.* **401,** 263 (1973).
11. Baker, L. M., and Carrick, W. L., *J. Org. Chem.* **33,** 616 (1968).
12. Krauss, H. L., and Stach, H., *Inorg. Nucl. Chem. Lett.* **4,** 393 (1968).
13. Groeneveld, C., dissertation, Technische Hogeschool Eindhoven, 1974.
14. Schimmel, A., Universität Bayreuth, unpublished.
15. Hums, E., dissertation, Universität Bayreuth, 1980.