

Effect of Hydrogen on the Ethylene Polymerization Process over Ziegler–Natta Catalysts Supported on $\text{MgCl}_2(\text{THF})_2$.

I. Studies of the Chain-Transfer Reaction

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ABSTRACT: The effect of hydrogen on the molecular weight of polyethylene obtained over vanadium catalysts (based on VCl_4 and VOCl_3) supported on $\text{MgCl}_2(\text{THF})_2$ was studied and the results were compared to those obtained for similar titanium catalysts. It was confirmed that the dependencies of the transfer reaction on the hydrogen concentration are a half-order in all investigated systems. However, the transition metal of the catalytic site affects the ratio of the transfer rate with hydrogen to the propagation rate ($k_{\text{tr,H}}/k_p$) and the results showed that hydrogen is a more effective agent of polyethylene molecular weight control in vanadium-based systems as compared to the titanium catalyst. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 356–360, 2001

Key words: ethylene polymerization; vanadium and titanium catalysts; hydrogen; molecular weight; chain transfer with hydrogen

INTRODUCTION

Organometallic vanadium-based catalysts supported on the complex of magnesium chloride with tetrahydrofuran (THF) and activated with diethylaluminum chloride, that is, $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$ and $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$, turned out to be very active and stable in the ethylene polymerization process.^{1–4} These catalysts can produce a polymer with very high molecular weight, of the order of a few million,^{1,5} which has a number of favorable physical–chemical and mechanical properties. On the other hand, however, its rheology and processing properties are inferior.^{6,7} Also, the solubility of this polymer is considerably limited, which makes its complete

molecular specification impossible, including determination of its molecular weight and molecular weight distribution using gel permeation chromatography (GPC). Hence, the molecular weight of polyethylene has to be controlled in the synthesis process.

Hydrogen is the only commercially applicable chain-transfer agent in the low-pressure olefin polymerization process over the Ziegler–Natta catalysts.^{8,9} It was observed that hydrogen has a large effect not only on the product molecular weight but also on the catalyst activity. In the presence of hydrogen, the activity of TiCl_3 , MgCl_2 -supported, and metallocene catalysts decreases clearly in the polymerization of ethylene, but different effects were observed in the polymerization of propylene. The activity of $\alpha\text{-TiCl}_3$ - and Al-alkyls-based catalysts is also inhibited, although, on the other hand, a remarkably activating effect of hydrogen was more frequently observed for various MgCl_2 -supported and metallocene cata-

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lytic systems.⁹ Thus, the effect of hydrogen on the polymerization of ethylene is not so clear. This effect was found to be dependent on the type of catalyst, cocatalyst, monomer, and polymerization conditions. The subject of this work was an investigation of the hydrogen impact on the ethylene polymerization process over two vanadium-based catalysts supported on the magnesium chloride-THF complex and a comparison to a similar study which involved the titanium catalyst supported on the same magnesium complex: $\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4/\text{Et}_2\text{AlCl}$.¹⁰

EXPERIMENTAL

A supported magnesium-vanadium-aluminum catalyst was prepared by depositing—with the use of a milling technique—the vanadium compound VCl_4 or VOCl_3 on the $\text{MgCl}_2(\text{THF})_2$ support and subsequent activation with diethylaluminum chloride. The materials used, the catalyst synthesis, and the ethylene polymerization procedures adopted were specified in our previous articles.¹⁻⁴

Molecular weights of the obtained polymers were determined by the viscosity method in decaline at 135°C and using the relationship $[\eta] = 1.16 \times 10^{-4} M_v^{0.8}$ (ref. 11) or by the GPC method with a Waters instrument, Model 150-C. The operating conditions of the GPC method were described in ref. 12. The molecular weight distributions (MWDs) and average molecular weights were determined using the universal calibration curve obtained with narrow MWD polystyrene standards.

RESULTS AND DISCUSSION

The effect of hydrogen on the ethylene polymerization process and on the molecular weight (\overline{M}_v) of the products obtained was studied by changing the hydrogen share in the gas phase from 9 to over 50% vol while maintaining the other process parameters unchanged. The results as presented in Figure 1 confirm that hydrogen is an efficient chain-transfer agent for the vanadium systems studied. The increased hydrogen share in the polymerization feed gives, clearly, a lower molecular weight of the polyethylene produced. Only 10% of hydrogen in the gas phase results for both the catalysts in the nearly 10 times lower \overline{M}_v of polyethylene. Hence, the ethylene polymerization pro-

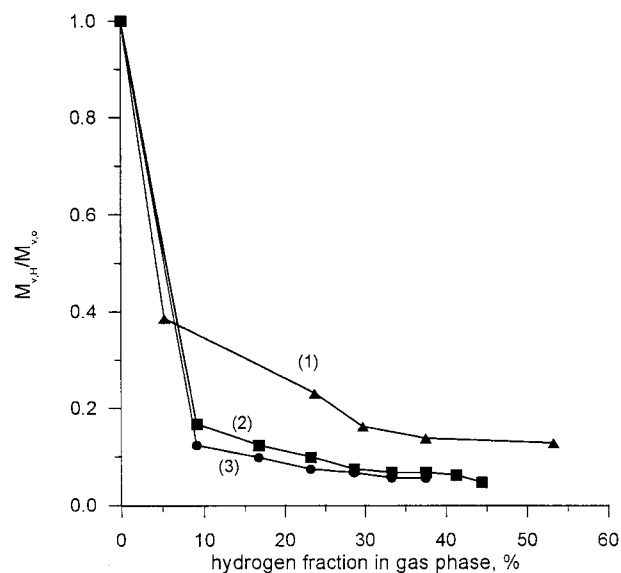


Figure 1 Effect of hydrogen on molecular weight of polyethylene obtained on catalysts: (1) $\text{MgCl}_2(\text{THF})_2/\text{TiCl}_4/\text{Et}_2\text{AlCl}$; (2) $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$; (3) $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$. Polymerization conditions are the same as those described in Table I.

cess carried out in the presence of the vanadium catalysts can yield polyethylene with a molecular weight from a few million to about 100,000, depending on the polymerization conditions and amounts of hydrogen introduced. These results can be compared to our earlier results¹⁰ obtained for the titanium catalyst supported on the same magnesium complex. The comparison shows (Fig. 1) a clearly higher effect of hydrogen in the case of the vanadium catalysts than for their titanium equivalent. In the latter case, even 50% hydrogen in the gas phase lowers the polyethylene molecular weight to just below 1 million. These results are similar to those presented in ref. 13 where the hydrogen effects were compared in the ethylene polymerization processes over titanium and vanadium catalysts supported on highly dispersed magnesium chloride.

Such a substantial decrease of the polyethylene molecular weight in the case of the studied vanadium catalysts enabled the molecular specification of the produced polyethylenes using the GPC method (Fig. 2). Both catalysts studied were found to yield polyethylenes with similar polydispersity, that is, having Q values of about 7 ($Q = \overline{M}_v/\overline{M}_n$), which was only slightly higher than those obtained for the corresponding titanium catalyst ($Q =$ about 6).¹⁴ These results reveal clearly a narrower MWD for polyethylene pro-

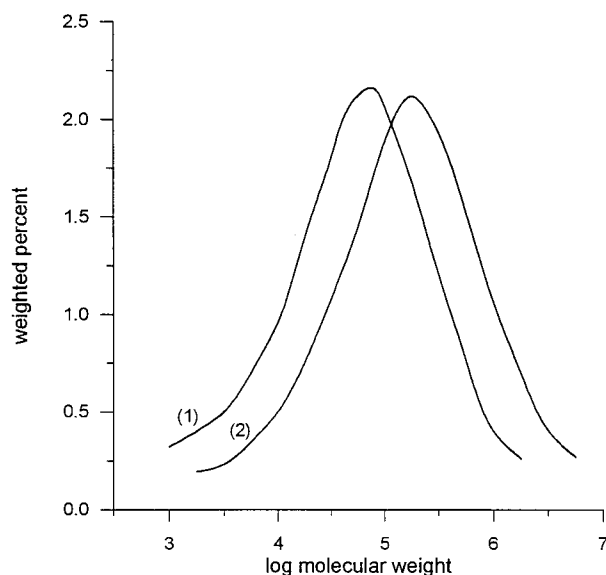


Figure 2 GPC distribution plots for polyethylene obtained on the catalyst $\text{MgCl}_2(\text{THF})_2/\text{VOCl}_3/\text{Et}_2\text{AlCl}$. The hydrogen share in the gas phase in % (v/v): (1) 33.3; (2) 9.1. Polymerization conditions are the same as those described in Table I.

duced with the use of the presently studied catalysts as compared to those described in ref. 13 for similar systems supported on highly dispersed magnesium chloride ($Q = 20$ for the vanadium catalysts and $Q = 7$ for the titanium catalyst). This may suggest that the use of $\text{MgCl}_2(\text{THF})_2$ as the vanadium catalyst support instead of MgCl_2 gives the systems with superior homogeneity of active sites.

The effect of hydrogen on the chain-transfer reaction in the olefin polymerization process is not completely clear. It is known that the chain-transfer reaction by hydrogen occurs as follows¹⁵:



with subsequent insertion of the monomer into the bond formed between the catalyst metal and hydrogen:



A proportional decrease of the polymer molecular weight with increase of the hydrogen pressure is usually observed for homogeneous systems^{16,17}; this is in conformance with eq. (1). However, in

heterogeneous catalysis, Natta^{18,19} and many researchers²⁰⁻²⁶ found that the observed dependencies of the chain-transfer reaction on hydrogen pressure are not of first order but of half-order. Natta,¹⁸ on the basis of these results, suggested that the transfer reaction followed the dissociative adsorption of hydrogen on active sites. These conditions, however, are not always satisfied. There are cases known where the chain-transfer reaction with the use of hydrogen in the heterogeneous systems follows the I-order scheme.^{13,19,20,27} On the other hand, it was noticed²⁸ that molecular hydrogen was involved in the isotactic polypropylene chain-transfer reaction and atactic macromolecules were terminated with hydrogen atoms. The transfer reaction rate with hydrogen can be described by the following relationship:

$$R_{\text{tr,H}} = k_{\text{tr,H}} [C_t^*][\text{H}_2]^\alpha \quad (3)$$

where $R_{\text{tr,H}}$ is the transfer reaction rate with hydrogen; $k_{\text{tr,H}}$, the constant of the transfer reaction rate with hydrogen; $[C_t^*]$, the concentration of active sites at time t ; $[\text{H}_2]$, the hydrogen concentration; and α , the unknown order of the transfer reaction with hydrogen.

At the same time, the dependence is known from the Natta and Pasquon study¹⁹ between the polymerization degree and the ratio of propagation and chain-termination rates. The chain-transfer reaction both with the monomer and hydrogen are responsible for the polymer chain termination because the systems studied are stable in the course of polymerization^{2,3}:

$$\frac{1}{DP_{n,H}} = \frac{k_{\text{tr,M}}[C_t^*][M] + k_{\text{tr,H}}[C_t^*][\text{H}_2]^\alpha}{k_p[C_t^*][M]} \quad (4)$$

where: $DP_{n,H}$ is the number-average degree of polymerization in the presence of H_2 ; $k_{\text{tr,M}}$, the constant of the transfer reaction rate with the monomer; k_p , the propagation rate constant; and $[M]$, the monomer (ethylene) concentration. Since the equation for the polymerization without hydrogen is

$$\frac{1}{DP_{n,0}} = \frac{k_{\text{tr}}[C_t^*][M]}{k_p[C_t^*][M]} \quad (5)$$

then

$$\frac{1}{DP_{n,H}} = \frac{1}{DP_{n,0}} + \frac{k_{\text{tr,H}}[C_t^*][\text{H}_2]^\alpha}{k_p[C_t^*][M]} \quad (6)$$

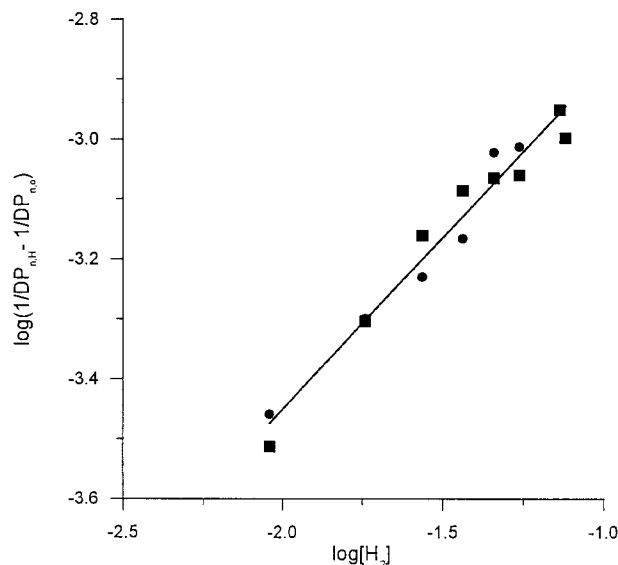


Figure 3 $\log(1/DP_{n,H} - 1/DP_{n,0})$ versus $\log[H_2]$ according to eq. (8) for the supported vanadium catalysts: (●) $MgCl_2(THF)_2/VOCl_3/Et_2AlCl$; (■) $MgCl_2(THF)_2/VCl_4/Et_2AlCl$. Polymerization conditions are the same as those described in Table I.

and

$$\frac{1}{DP_{n,H}} - \frac{1}{DP_{n,0}} = \frac{k_{tr}}{k_p[M]} [H_2]^\alpha \quad (7)$$

After finding the logarithm of eq. (7), one obtains a linear dependence between the polymer molecular weight (polymerization degree) and the concentration of hydrogen in the reaction medium:

$$\log\left(\frac{1}{DP_{n,H}} - \frac{1}{DP_{n,0}}\right) = \log\frac{k_{tr}}{k_p[M]} + \alpha \log[H_2] \quad (8)$$

As illustrated in accordance with eq. (8) in Figure 3, our results give similar and linear dependencies for both catalysts. Their slopes correspond to the order of the chain-transfer reaction with hydrogen and the abscissae enable one to calculate the ratio of the rate constant to the propagation rate constant, that is, the value of $k_{tr,H}/k_p$ with the monomer concentration taken into consideration. For need of comparison, similar calculations were performed for earlier¹⁰ dependencies of the average-viscosity molecular weight of polyethylene (\bar{M}_v) versus the hydrogen concentration for equivalent titanium catalysts. The use of available results for \bar{M}_v instead of \bar{M}_n requires that the polydispersity index Q (ref. 13) must be added to eq. (8):

$$\log\left(\frac{1}{DP_{v,H}} - \frac{1}{DP_{v,0}}\right) = \log\frac{k_{tr}}{k_p O[M]} + \alpha \log[H_2] \quad (9)$$

The calculation results as provided in Table I confirm that the reaction order for the chain-transfer reaction with hydrogen is close to 0.5 for the studied systems supported on $MgCl_2(THF)_2$. This is not in conformance with the calculation for the similar systems supported on $MgCl_2$.¹³ However, a good coincidence is found for most results for heterogeneous systems. The data presented suggest that hydrogen is adsorbed dissociatively on active sites and forms active hydrides, for example, transition-metal-hydrogen, conducive for insertion of the monomer and transfer of the growing chain. Additionally, as in ref. 13, we found the order of the reaction studied to be not dependent on the type of transition metal used in a precatalyst. However, the metal affects the ratio of the transfer rate with hydrogen to the propa-

Table I Effect of Hydrogen on Transfer Reaction of Polyethylene Growing Chain over Ziegler-Natta-type Catalysts Supported on $MgCl_2(THF)_2$

Precatalyst	Results According to eq. (8) or (9)			
	$k_{tr,H}/(k_p[M])$	α	r	$k_{tr,H}/k_p$
$MgCl_2(THF)_2/VOCl_3^a$	5.15×10^{-3}	0.58	0.98	2.50×10^{-3}
$MgCl_2(THF)_2/VCl_4^a$	4.89×10^{-3}	0.57	0.99	2.34×10^{-3}
$MgCl_2(THF)_2/TiCl_4^b$	$5.22 \times 10^{-5}^c$	0.55	0.98	—

^a Polymerization conditions: $[VOCl_3] = 0.015 \times 10^{-3}$ mol/dm³ or $[VCl_4] = 0.015 \times 10^{-3}$ mol/dm³; $[Et_2AlCl] = 25 \times 10^{-3}$; $p_{Et} = 0.5$ MPa; $T = 33^\circ\text{C}$.

^b Polymerization conditions: $[Ti] = 0.135 \times 10^{-3}$ mol/dm³; $[Et_2AlCl] = 81 \times 10^{-3}$ mol/dm³; $p_{Et} = 0.28$ MPa; $T = 50^\circ\text{C}$.

^c $k_{tr}/(k_p[M]Q)$.

gation rate ($k_{tr,H}/k_p$) (Table I), which becomes visible by the higher efficiency of hydrogen as the molecular weight control agent in vanadium-based systems as compared to titanium catalysts.

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