Chlorinated organic polymers as supports for Ziegler–Natta catalysts

Soraya Jericó, Ulf Schuchardt *, Inés Joekes, Walter Kaminsky [1], Annegret Noll

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970 Campinas, SP, Brazil

Abstract

Chlorinated organic polymers were prepared, characterized and used as supports for $TiCl_4$. The activity of the new catalysts in the polymerization of ethylene was compared with that observed for $TiCl_4$ supported on non-chlorinated polymers. It was found that the new catalysts have initial activities of up to 4 kg PE/mol Ti·min·bar, but deactivate quickly, probably due to insertion of Ti(III) into the carbon–chlorine bonds. The viscosimetric average molecular weights of the PE produced with the new catalysts are between 300 and 550 kg/mol, in agreement with a short polymerization time.

Keywords: Chlorinated organic polymers; Ethylene; Polymerization; Supported catalysts; Ziegler–Natta catalysts

1. Introduction

The use of supports to improve the activity of Ziegler–Natta catalysts has been reported since the early sixties [1]. Such supports may be inorganic or organic. For α-olefin polymerization the supports used are almost entirely inorganic [2,3]. Nevertheless, organic polymers have shown to be a good option as the macromolecular structure of these supports influences the catalytic activity, selectivity and stereospecificity of the transition metal catalysts [4–6]. The presence of functional groups in the polymer structure is fundamental to promote chemical bonds or well defined interactions between the catalyst and the polymer. Functionalized polystyrenes are often used as supports [7–10], but poly(4-vinylpyridine) was shown to

be a good alternative for copper [11], cobalt [12] and nickel catalysts [13]. Both polymers have functional groups in their structures able to interact with transition metal catalysts. Cyclopentadienylmethyl substituted poly(styrene/divinylbenzene) (PScp) and poly(4-vinylpyridine/divinylbenzene) (P4VP) were used in this study for comparison with chlorinated polymers.

Polymers like atactic poly(propylene) (PP), natural rubber (NR) and poly(vinyl chloride) (PVC) have low surface free energies and no functional groups able to interact with Ziegler–Natta catalysts, but it is possible to introduce functional groups into the polymer [14]. It is known that catalytic systems containing chlorine in the support and/or in the co-catalyst show improved activity and/or better quality of the obtained polymer [1]. Chlorination of PP, NR and PVC was therefore accomplished and the chlorinated polymers were used for heterogenization of Ziegler–

* Corresponding author. Fax. (+55-192)393805.
[1] Permanent address: Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, 20146 Hamburg, Germany.

Natta catalyst in order to study their activity in ethylene polymerization.

2. Experimental

2.1. Materials

Ethylene (Linde, 99.95%) was used after passing over a copper catalyst (BASF R3-11) and a 10 Å molecular sieve to remove O_2 and water. Argon was passed through an oxygen filter (Messer Griesheim). $TiCl_4$ (Aldrich 99.99%) and $Al(C_2H_5)_3$ (Schering AG) were commercial products and used without further purification. Toluene (Merck) and heptane (Fluka) were predried with KOH, refluxed over Na/K alloy and distilled under argon. The polymers used were atactic poly(propylene) (PP) (PPH-Cia Industrial de Polipropileno), natural rubber (NR) (Malaysia), poly(vinyl chloride) (PVC) (Aldrich), poly(chloromethylstyrene/2% divinylbenzene) (PS) (Aldrich, 1 mequiv. Cl/g, Merrifield polymer) and poly(4-vinylpyridine) with 2 or 25% divinylbenzene (P4VP 2% or P4VP 25%) (Fluka). The PP and NR were previously purified [15,16]. The other polymers were used without purification.

2.2. Support functionalization

A 1% (w/v) solution of NR or PP in carbon tetrachloride was kept at room temperature or at 50°C, respectively. In the presence of natural light, chlorine gas (Cl_2) was bubbled slowly through the solution during 4 h. During the chlorination, the hydrochloric acid and the excess chlorine were absorbed in a 30% sodium hydroxide solution.

Two g of PVC were dissolved in 150 ml of chlorobenzene at 80°C. One ml of sulfuryl chloride and 1–2 mg of azobisisobutyronitrile were added. The solution was kept at this temperature for 20 h [17].

The chlorinated polymer solutions were sprinkled into ethanol using a flow sparger [18]. The polymers were separated from the solvent by filtration and dried under vacuum. The materials were pulverized with a ball mill and passed through a 42 mesh sieve. After drying under vacuum at 50°C, the polymers were kept under argon.

The Merrifield polymer (PS) was functionalized with cyclopentadiene to give PScp, using the method described by Grubbs et al. [19]. The P4VP 2% and 25% were used after drying under vacuum at 50°C.

The surface areas of the polymers were determined by N_2 adsorption isotherms using a Carlo Erba Sorptomatic BET instrument.

2.3. Catalyst preparation

All reactions were carried out under an argon atmosphere. Approximately 3 g of the dried polymer was suspended in 50 ml of n-heptane at 50°C. Three ml of a 0.94 M heptane solution of $TiCl_4$ ($2.8 \cdot 10^{-3}$ mol) was added and the suspension was stirred for 1 h. The catalyst was washed 5 times with heptane and dried in vacuum.

For the heterogenization of $TiCl_4$ on PScp, 1 g of the polymer in 10 ml of toluene was treated with 0.8 ml of a 2.5 M heptane solution of butyllithium ($2.0 \cdot 10^{-3}$ mol). After stirring overnight, the polymer was filtered and washed 5 times with 10 ml toluene. The polymer was then treated with 2 ml of a 1 M solution of $TiCl_4$ in toluene ($2.0 \cdot 10^{-3}$ mol). The suspension was stirred overnight. The catalyst was washed 5 times with 10 ml toluene and dried in vacuum.

For titanium determination the polymer supported catalysts were dissolved in a Kjeldahl apparatus in a mixture of conc. nitric and sulfuric acid (2:1, v:v). The reacted catalysts were diluted with bidistilled water to complete 100 ml. These solutions were analysed with a Perkin Elmer ICP/6000 optical emission spectrophotometer with a Perkin Elmer 7500 data station, using an inductive coupled plasma (ICP-OES) operating under the following conditions: 14 l/min of argon flow, 2 bar of gas pressure, Perkin Elmer cross-flow pulverization. A standard solution (Aldrich) of 1000 μgTi/ml in 5% HCl was used for calibration.

2.4. Ethylene polymerization

Polymerization reactions were carried out in an 1 l glass reactor (Büchi) with mechanical stirring. Heptane (100 ml) and 1 ml of the neat co-catalyst ($AlEt_3$, $AlMe_3$, $AlBu_3$ or Me_2AlCl) were introduced under argon. Approximately 300 mg of the catalyst were added. The reactor was closed and 2 bar of ethylene were introduced. The reactions were usually carried out for 10 min or 1 h at 50°C. Ethylene consumption during the polymerization was monitored in terms of the weight loss of the lecture bottle, placed on a balance. To ensure reproducibility of the polymerizations, all reactions were repeated at least 3 times. After 1 h, the reactor was evacuated, the polymerization quenched with ethanol and the polymer stirred with a solution of aqueous HCl (37%)/ethanol (1:3, v:v) overnight. The filtered polymer was then washed with excess of water and dried under vacuum.

The viscosimetric molecular weight (M_v) of the polymers was determined using a Ubbelohde viscosimeter and a Lauda Viskoboy. The polymers were dissolved in decalin, the catalyst was filtered off and the viscosity was measured at 135°C. The IR spectra were recorded as a Nujol suspension (catalysts) or as KBr pellets (polymeric supports) using a Nicolet FT-IR 20 SXB spectrometer.

3. Results and discussion

Poly(vinyl chloride), after chlorination to PVC–Cl, is a white powder and showed no changes in its morphology. On the other hand, both poly(propylene) and natural rubber, after chlorination to PP–Cl and NR–Cl, lost their waxy, elastomeric properties, becoming white and hard. A fine powder was obtained using a flow sparger for precipitation.

The chlorine content of the chlorinated polymers (Table 1) indicates that the substitution by chlorine atoms in NR–Cl is 2.5 times higher than in PP–Cl and PVC–Cl. The chlorine content in PP–Cl can be determined from the concentration of the polymer solution. In more dilute solutions, the mobility of the polymer chains is higher favoring the diffusion of the chlorine radicals to the polymer [20]. As the substitution degree is 1.4 chlorine atoms per monomeric unit (Table 1) and the sequence of hydrogen per chlorine exchange in the hydrocarbon is tert > sec > primary [20], we suppose that the substitution first occurs at the methyne and then at the methylene groups (Scheme 1). The PP–Cl should, therefore, have an intermediate structure between **a** and **b**. Substitution at the methyl groups probably does not take place as there is not an excess of chlorine. The IR spectrum of PP–Cl shows an intense C–Cl stretching band at 750–800 cm^{-1}. Due to the broadness of this band, one cannot differentiate between tertiary, secondary and primary C–Cl groups [21] (a). On the other hand, we observed a relative decrease in intensity of the bands at 840–810 cm^{-1} attributed to trisubstituted double bonds [22].

A radical mechanism for the chlorination of the natural rubber can be excluded, since light, peroxide and anti-oxidants do not influence the initial stage of chlorination [16]. Kinetic data show the formation of a molecular complex and subsequent
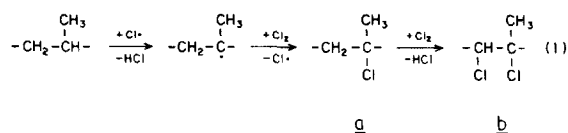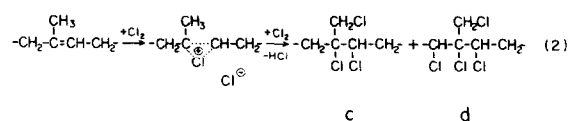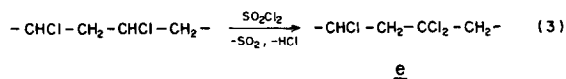
Scheme 1.

Table 1
Chlorine content in the chlorinated polymers

Polymer	Chlorine content (% w/w)	Substitution degree [a]
PP–Cl	55	1.4
NR–Cl	67	3.7
PVC–Cl	64	1.3

[a] Average number of chlorine atoms per monomeric unit.

Scheme 2.

$$- CHCl - CH_2 - CHCl - CH_2 - \xrightarrow[\text{-SO}_2, \text{-HCl}]{\text{SO}_2\text{Cl}_2} - CHCl - CH_2 - CCl_2 - CH_2 - \quad (3)$$

e

Scheme 3.

Table 2
Infrared Ti–Cl absorbance of TiCl₄ heterogenized on chlorinated polymers

Catalyst	σTi–Cl (cm^{-1})
PP–Cl/TiCl₄	409 and 353 (broad)
NR–Cl/TiCl₄	425 (broad)
PVC–Cl/TiCl₄	425 and 357 (broad)

heterolytic cleavage of the Cl–Cl bond and proton loss [16] (Scheme 2). The bands for trisubstituted olefins at 1665 cm^{-1} ($\nu_{C=C}$) and 840 cm^{-1} (γ_{CH}) [22] disappear in the IR spectrum of NR–Cl [21] (b). On the basis of approximately 3.7 chlorine atoms per monomeric unit (Table 1), NR–Cl structures like c and d should be present in the polymer.

Theoretically, up to 3 hydrogen atoms can be substituted in PVC, which would increase the chlorine content to 84%. However, a maximal chlorine content of 73% (2 atoms per monomeric unit) was reported by Sikorski and Czerwinska [17], who suggest that the methylene groups are predominately involved in the first stage of the chlorination. The chlorine content of PVC–Cl is 64%, being equivalent to 1.3 chlorine atoms per monomeric unit (Table 1). The IR spectrum of PVC–Cl shows some reduction of the intensity of the characteristic bands of the methylene groups (1430–1460 cm^{-1}). Additionally, new bands at 1580, 740 and 450 cm^{-1} are observed. The 450 cm^{-1} IR absorbance is related to CCl₂ and appears

in PVC–Cl with high chlorine content [17]. We, therefore, believe that chlorination of PVC takes place predominantly at the CHCl group, leading to structure e (Scheme 3).

Heterogenization of TiCl₄ on the chlorinated polymers changes the color from white to yellow-light brown. The absorption of δTi–Cl of TiCl₄ is observed at 499, 485 and 495 cm^{-1} in the vapor, liquid and solid state, respectively [23]. When the TiCl₄ is bound to the chlorinated polymers, these bands are broader and observed at lower frequencies, as shown in Table 2. The absorption bands of νC–Cl (between 800 and 750 cm^{-1}) also suffer a shift of approximately 15 cm^{-1} to lower frequency by complexation with TiCl₄. These bands are, however, more difficult to observe as the concentration of TiCl₄ on the samples is low.

After reaction with TiCl₄ the IR spectrum of poly(4-vinylpyridine) (P4VP) also shows changes in the absorption bands. The intensity of the absorption at 1595 cm^{-1}, which is due to the vibration of the pyridine ring skeleton, decreases and new absorptions at 1613 and 1633 cm^{-1} are observed. The shift of the 1595 cm^{-1} band to higher frequency is characteristic for complexation of a transition metal compound to the polymer [24]. The white P4VP becomes yellow after the heterogenization.

Poly(cyclopentadienylmethylstyrene/2% DVB) (PScp) suffers a color change from yellow to dark brown after heterogenization with TiCl₄.

The activity of TiCl₄ supported on the chlorinated polymers for ethylene polymerization in the presence of different co-catalysts is shown in

Table 3
Ethylene polymerization catalyzed by TiCl₄ supported on chlorinated polymers, using different co-catalysts

Support	Surface area (m^2/g)	[Ti] × 10^5 (mol Ti/g support)	Activity (kg PE/mol Ti·bar)				M_v [a] (kg/mol)
			AlMe₃	AlEt₃	AlBu₃	Me₂AlCl	
PP–Cl	45	5.7	12.4	20.7	20.2	9.6	303
NR–Cl	33	8.3	7.3	15.9	10.8	6.2	555
PVC–Cl	59	7.2	10.6	18.4	17.3	9.0	450

Polymerization conditions: 300 mg of catalyst, 1 ml of co-catalyst, 2 bar of ethylene, 10 min at 50°C.
[a] For the polymers obtained with AlEt₃.

Table 4
Ethylene polymerization catalyzed by $TiCl_4$ supported on non-chlorinated organic supports, using different co-catalysts

Support	Surface area (m^2/g)	[Ti] $\times 10^5$ (mol Ti/g support)	Activity (kg PE/mol Ti·bar)			M_v [a] (kg/mol)
			$AlMe_3$	$AlEt_3$	Me_2AlCl	
P4VP 2%	36	0.80	n.d.	2.5	n.d.	963
P4VP 25%	82	4.88	3.4	7.9	1.6	1059
PScp	34	5.98	1.1	1.7	n.d.	1488

Polymerization conditions: 300 mg of catalyst, 1 ml of co-catalyst, 2 bar of ethylene, 1 h at 50°C.
[a] For the polymers obtained with $AlEt_3$, n.d. = not determined.

Table 3. The catalysts on the less chlorinated supports show better activities. Although the PP–Cl heterogenizes the smallest quantity of $TiCl_4$, it shows the highest activity for ethylene polymerization with all co-catalysts. $TiCl_4$ heterogenized on PVC–Cl also shows good activities with the four co-catalysts studied. $TiCl_4$ on NR–Cl gives only reduced activity due to the high chlorine content of the polymer, which coordinates the reduced $TiCl_4$ more strongly, thus blocking coordination sites for ethylene. $AlEt_3$ is the best co-catalyst for all chlorinated catalytic systems, as expected from studies of $TiCl_4$ activation [25]. On the other hand, $AlBu_3$ gives good results while the methylated co-catalysts, $AlMe_3$ and Me_2AlCl, are less effective.

As the quantity of $TiCl_4$ heterogenized under reaction conditions on the same polymers without chlorination was very small, these materials were not considered suitable supports for comparison. We, therefore, compared the activity of $TiCl_4$ supported on the chlorinated polymers with that of $TiCl_4$ on the non-chlorinated polymers PScp and P4VP which bind $TiCl_4$. The results obtained are shown in Table 4. The activity of the catalysts depends on the surface area and the rigidity of the support. Macroporous P4VP (25% DVB) has a high surface area and, consequently, a high quantity of exposed functional groups for heterogenization. This not only allows the easy heterogenization of $TiCl_4$ but also results in good catalytic activity. On the other hand, $TiCl_4$ sup-

ported on microporous P4VP (2% DVB) shows low activity due not only to a low concentration of the catalyst, but also to the mobility of the polymer chains, obstructing the active sites. Although PScp heterogenizes $TiCl_4$ effectively, the activity of the catalyst is low when compared with $CpTiCl_3$ [26]. This is probably also due to the mobility of the polymer chains which obstructs active sites. In general, the activity of $TiCl_4$ heterogenized on the non-chlorinated polymers is much lower than that observed for $TiCl_4$ on the chlorinated polymers.

The kinetics of the polymerization reactions were followed by the weight loss of the ethylene lecture bottle. In this way, a very rapid ethylene uptake was initially observed for $TiCl_4$ supported on the chlorinated polymers, which diminished quickly, reaching zero after approximately 10 min. On the other hand, the ethylene uptake of $TiCl_4$ supported on the non-chlorinated polymers was much slower and only ceased after approximately 1 h.

The rapid deactivation of $TiCl_4$ on the chlorinated polymers could be interpreted as an oxidative addition of the support to the catalyst. The Ti(III), present after reduction with the aluminumalkyls, cleaves carbon–chlorine bonds of the polymer [2] giving a polymeric Ti(IV) complex which is not active (Scheme 4). An attack of the co-catalyst at the electrophilic carbons of the polymer chain [27] would also explain the rapid deactivation of the catalyst, but seems less probable.

$$-\overset{|}{\underset{|}{C}}- \ + \ 2\ TiCl_3 \ \longrightarrow \ -\overset{|}{\underset{|}{C}}- \ + \ TiCl_4 \quad (4)$$
$$Cl TiCl_3$$
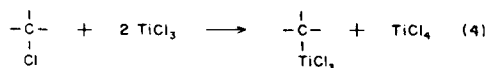
Scheme 4.

[2] $TiCl_3$ reacts with alkyl chlorides forming colorless Ti(IV) compounds.

The viscosimetric average molecular weights (M_v) of the polymers confirm this observation. While the average molecular weights of the PE obtained with $TiCl_4$ on the chlorinated polymers are relatively small, due to the short polymerization time, those of the PE obtained with $TiCl_4$ on the non-chlorinated polymers are 1000 kg/mol or higher, in agreement with the longer polymerization time (Tables 3 and 4).

The $TiCl_4$/P4VP 25% DVB system has a high stability. After 135 days of storage the catalyst has a similar activity to that observed for the freshly synthesized catalyst. On the other hand, the $TiCl_4$ supported on PP–Cl shows loss of activity after 1 week, which reflects the sensitivity of the new catalyst.

To the best of our knowledge there are no reports in the literature about similar Ziegler–Natta catalysts supported on chlorinated polymers. Some results of Ziegler–Natta catalysts supported on non-chlorinated polymers are described. Titanium tetraisopropoxide heterogenized on PScp shows an activity of 140 kg PE/mol Ti·h·bar [5]. However the polymerization conditions are very drastic, since high pressure and temperature were used. PS without previous functionalization was recently used as support of $TiCl_4$ for isoprene polymerization [9], obtaining slightly higher catalytic activity than for the unsupported catalyst. A mixture of P4VP and the terpolymer ethylene/propylene/unconjugated diene has also been used as support for $TiCl_4$. The activity of this catalyst for ethylene polymerization at 40°C and 3 bar of ethylene was 0.7 kg PE/mol Ti·h·bar [28]. This activity is lower than that obtained by us for P4VP 25% DVB and even for P4VP 2% DVB, indicating that the swelling of the terpolymer rubber obstructs the coordination sites, thus reducing the catalytic activity.

4. Conclusions

Chlorinated organic polymers, when used as support, confer to $TiCl_4$ a high initial activity for ethylene polymerization of up to 4 kg PE/mol Ti·min·bar, compared to 2–15 kg PE/mol Ti·min·bar typically observed for $TiCl_4$ supported on $MgCl_2$ [2]. On the other hand, the new catalysts deactivate much more quickly, probably due to insertion of Ti(III) into the carbon–chlorine bonds of the polymers. The average molecular weights of the PE produced with the new catalysts are, therefore, relatively low.

Acknowledgements

References

[1] P. Pino and R. Mülhaupt, Angew. Chem. Int. Ed. Engl., 19 (1980) 857.

[2] P.D. Gavens, M. Bottrill, J.W. Kelland and J. McMeeking, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 3, Pergamon Press, Oxford, 1982, p. 475.

[3] J. Boor, Jr., Ziegler–Natta Catalysts and Polymerization, Academic Press, New York, 1979.

[4] Y. Li and J. Ouyang, J. Macromol. Sci.-Chem., A24 (1987) 227.

[5] S.A. Bedell, W.R. Howell, Jr. and W.M. Colemann III, U.S. Pat. Appl., US 4,632,912 (1986); Chem. Abstr., 106 (1987) 120392.

[6] A.M. Bochkin, A.D. Pomogailo and F.S. D'yachkovskii, Polym. Sci. USSR, 29 (1987) 1485.

[7] P.E. Garrou and B.C. Gates in D.C Sherrington and P. Hodge (Eds.) Syntheses and Separations using Functional Polymers, John Wiley and Sons, New York, 1988, p. 123.

[8] D.E. Bergbreiter, ACS Symp. Ser., 308 (1986) 17.

[9] R. Ran, J. Polym. Sci. Part A: Polym. Chem., 31 (1993) 1561.

[10] R. Ran., D. Fu, J. Shen and Q. Wang, J. Polym. Sci. Part A: Polym. Chem., 31 (1993) 2915.

[11] A.J. Moffat, J. Catal., 18 (1970) 193.

[12] E. Tsuchida, M. Kaneko and H. Nishide, Makromol. Chem., 64 (1973) 203.

[13] U. Schuchardt, E.N. dos Santos and F.S. Dias, J. Mol. Catal., 55 (1989) 340.

[14] D.D. Whitehurst, CHEMTECH, (1980) 44

[15] E.A. Collins, J. Bares and F.W. Billmeyer, Jr., Experiments in Polymer Science, John Wiley and Sons, New York, 1973, p. 64.

[16] L.B. Krentsel, S.O. Travin, A.D. Litmanovich and K.K. Yutujan, Eur. Polym. J., 21 (1985) 405.

[17] R.T. Sikorski and E. Czerwinska, Eur. Polym. J., 22 (1986) 179.

[18] E. Sabadini, Master's Thesis, Universidade Estadual de Campinas, 1988.

[19] W.D. Bonds, Jr., C.H. Brubaker, E.S. Chandrasekaran, C. Gibbons, R.H. Grubbs and L.C. Kroll, J. Am. Chem. Soc., 97 (1975) 2128.

[20] A.K. Mukherjee and M. Patri, Angew. Makromol. Chem., 163 (1988) 23.

[21] D.O. Hummel, F. Scholl, Atlas of Polymer and Plastics Analysis, Vol. 2 Part b/I, VCH Verlagsgesellschaft, Weinheim, 1988, (a) p. 350; (b) p. 353.

[22] N.B. Colthup, L.H. Daly and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, 1975, p. 376.

[23] M.F. Dove, J.A. Creighton and L.A. Woodward, Spectrochim. Acta, 18 (1962) 267.

[24] O.S. Roshchupkina, A.P. Lisitskaya and N.D. Golubeva, Kinet. Catal., 23 (1982) 1027.

[25] H. Sinn and W. Kaminsky, Adv. Organomet. Chem., 18 (1980) 99.

[26] P.C. Wailes, R.S.P. Coutts and H. Weigold, Organometallic Chemistry of Titanium, Zirconium, and Hafnium, Academic Press, London, 1974, p. 191.

[27] E.-I. Negishi, Organometallics in Organic Synthesis, Vol. 1, John Wiley and Sons, New York, 1980, p. 365.

[28] V.A. Kabanov, V.I. Smetanyuk, V.G. Popov, M.A. Martynova and M.V. Ul'yanova, Polym. Sci. USSR, 22 (1980) 372.