Effect of Halocarbon Promoters on Polyethylene Properties Using MgCl$_2$ (Ethoxide Type)/TiCl$_4$/AlEt$_3$/H$_2$ Catalyst System

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ABSTRACT: In our previous study we found that addition of proper amount of halocarbons (HC) including chlorocyclohexane (CHC), chlorocyclopentane (CHP), butylchloride (BC), 1,4-dichlorobutane (DCB), and chloroform (C) to the MgCl$_2$ (Ethoxide type)/TiCl$_4$/AlEt$_3$ catalytic system leads to a strong productivity improvement. In this study, the effect of these halocarbons on the properties of resulting polymers was investigated using H$_2$ as chain transfer agent at optimum HC/Ti molar ratio. The nature of halocarbon compound had a strong effect on polymer properties as well as on development of polymerization activity. Effect of halocarbon promoters on the polymer melt flow index (MFI), melt flow ratio (MFR), particle size distribution (PSD), bulk density, wax amount, crystallinity, and thermal properties of the poly-

mers were studied. Results showed that, in the presence of halocarbons, polyethylenes with higher MFI and bulk density, broader MFR and lower wax amount have been obtained. Also, sieve analysis showed that, in the presence of halocarbons as promoter, polymers had better particle size distribution (PSD). DSC analysis showed that the T_m of PEs prepared with the different promoters were in the region commonly reported for HDPE and was not affected substantially by halocarbons, but, the crystallinity of the polymers has been improved using halocarbon promoters. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1780–1786, 2010

Key words: Ziegler-Natta; polymerization; halocarbon; promoter; polymer properties

INTRODUCTION

It is well known that Ti/Mg catalyst systems are commonly used in production of polyethylene in industry. The relevant researches are focused on catalytic activity, particle morphology, particle size distribution, hydrogen response and copolymerization performance.[1,2] For slurry phase polymerization processes of ethylene, besides the requirement of higher activity catalyst, the control of the particle size and its distribution of the resultant polyethylene are quite important.

Halocarbon promoters are typically halogenated carbon compounds added directly to the polymerization reaction and are used to increase the catalytic activity. The use of halogenated hydrocarbons with titanium containing Ziegler-Natta catalysts for the

production of polyethylene was disclosed in some patents.[3,4] In general, it is disclosed that the halogenated hydrocarbons may reduce the rate of ethane formation, control the molecular weight of the polyethylene, produce polyethylenes with broad molecular weight distributions and provide other effects. Processing characteristics can be improved by broadening molecular weight distribution. For example, polyethylene having a broad molecular weight distribution is advantageously processed during the extrusion process, and in blow molding, polyethylene having a broad molecular weight distribution obtains an extruded product of increased strength.

It is known that the molecular weight of polyethylene may be controlled by the addition of a halocarbon to a catalyst system comprising a catalyst of a compound of a metal of Groups IVb, Vb, and VIb and organometallic compounds.[5]

Koch et al. found that by introducing halogenated hydrocarbon into the reactor, in slurry polymerization of ethylene using Ziegler-Natta catalysts, it is possible to reduce the proportion of components having a number of repeating units below 50 in the reactor and also in the flash tank. It is further stated as the byproduct suppressor

(halogenated hydrocarbon), which also increased polymerization activity by 20%, compared with an identical polymerization where the byproduct suppressor was not present.[6]

Halocarbons have been employed for improving tacticity of polymer product. Miller disclosed that certain halogenated halocarbons can be usefully employed in combination with a Ziegler-type catalyst comprising an organoaluminium compound and a titanium metal halide for the production of highly isotactic polypropylene.[7]

In this work, Ziegler–Natta heterogeneous supported catalyst was synthesized from $TiCl_4$ and magnesium ethylate with $MgCl_2$ *in situ* generation. Then, the effect of halocarbon compounds including chlorocyclohexane, chlorocyclopentane, butylchloride, 1,4-dichlorobutane, and chloroform on polymer properties at optimum amounts of HC/Ti molar ratios have been investigated.

EXPERIMENTAL

Materials

Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical (Tehran, Iran) and was used without further purification. Nitrogen gas (purity 99.99%) was supplied by Roham Co. (Tehran, Iran). $Mg(OEt)_2$, $TiCl_4$, and all halocarbons were purchased from Merck chemical (Darmstadt, Germany) and were used as received. *n*-Heptane supplied by Arak Petrochemical and was distilled over calcium hydride and stored over sodium wire and 13X and 4 Å activated molecular sieves. Triethylaluminum (TEAL) was acquired from Schering Co., (Bergkman, Germany).

Instruments

Surface area of the catalyst was determined using BET method by Quantachrome Corp. Nova2200, Version 7.11. For determination of Ti amount, after sample digestion in H_2SO_4, Ti was oxidized with H_2O_2 and analyzed by visible spectrophotometry ($\lambda = 410$ nm) in a spectrophotometer from Shimadzu 6800. The Cl amount was determined by the classic method of precipitation of AgCl with $AgNO_3$ (Volhard's method). Mg was determined by titrometry of the catalyst acidic solution with EDTA.

The DSC tests were performed on a DSC Q 1000 of TA, with samples of about 5 mg sealed in aluminum pans, under nitrogen atmosphere in a temperature range between 20 and 180°C, at a heating rate of 10°C/min. The melting and crystallization enthalpy and melting temperature of the samples were determined.

Melting temperature (T_m) and degree of crystallinity (X_c) were reported from the first heating scan (T_{m1}, X_{C1}) and from the second scan (T_{m2}, X_{C2}).

The degree of crystallinity was calculated via the total enthalpy method, according to the following eq:

$$X_C = \frac{\Delta H_m}{\Delta H_m^+}$$

where X_C is the degree of crystallinity, ΔH_m the specific enthalpy of melting, and ΔH_m^+ is the specific melting enthalpy for 100% crystalline PE. We used a ΔH_m^+ value of 288 J/g.[8,9]

As specified in the ASTM test D1238, melt flow index (MFI) of polyethylene was measured with a weight of 2.16 kg (MFI_2) and 10.00 kg (MFI_{10}) at 190°C; the results were expressed in grams per 10 min. The MFI_{10}/MFI_2 ratio was referred to as the melt flow ratio (MFR).

To measure PSD of the polymers sieve analysis has been employed. The sieve stack consisted of 0.01, 63, 125, 250, 425, 560, and 710 μm diameters. Sieves are normally considered to measure the distribution for sieve stack.

The soluble part of the polymers or wax amount was obtained by the extraction of the soluble part with boiling *n*-heptane for 2 h by means of Soxhlet extraction. The addition of the PE was about 0.5 g, which was put into a thimble. The insoluble part of the polymers left in the thimble were dried in oven overnight to obtain the wax amount, corresponding to the proportion of material extracted from the initial polymer.

Synthesis of catalyst precursor

Magnesium ethylate (114.3 g) was dispersed, under a blanket of N_2, in 1.5 L of a diesel oil fraction in a 3 L four-necked flask equipped with a dropping funnel, a stirrer, a reflux condenser, and a thermometer. Titanium tetrachloride (332 g) was added dropwise at 90°C to this dispersion in the course of 2 h. The reaction product was then washed with the diesel oil fraction until the supernatant solution no longer contained any titanium and then dried. Elemental analysis of the catalyst was: Ti = 3.43%, Mg = 21.29%, and Cl = 55.63%.

Polymerization experiments

The tests of ethylene polymerizations were carried out under slurry conditions at constant pressure and temperature in a 1 L Buchi stainless steel reactor equipped with a mechanical stirrer. Polymerization temperature was controlled by the circulation of water using a Huber circulator, model Polysat CC3.

TABLE I
Promotion Effect of Various Halocarbons on $MgCl_2$ (Ethoxide type)/$TiCl_4$/$AlEt_3$ Catalyst System in Ethylene Polymerization

Halocarbon type	HC/Ti (molar ratio)	Activity (Kg PE/gr Cat.h) (H_2/Et = 0/8.5)	Increase in activity (%) (H_2/Et = 0/8.5)	Activity (Kg PE/gr Cat.h) (H_2/Et = 5/3.5)	Increase in activity (%) (H_2/Et = 5/3.5)
Chlorocyclohexane	0	16.88	0	10.50	0
	128	31.18	84.72	20.43	94.57
Chlorocyclopentane	0	16.88	0	10.50	0
	110	30.54	80.92	19.50	85.71
Butylchloride	0	16.88	0	10.50	0
	20	27.86	65.05	17.47	66.38
1,4-Dichlorobutane	0	16.88	0	10.50	0
	0.54	28.70	70.02	17.71	68.67
Chloroform	0	16.88	0	10.50	0
	0.033	28.07	66.29	17.80	69.52

Polymerization Conditions are: P: 8.5 bar, T: 83°C, t: 1 h, Al/Ti = 180.

Before each polymerization experiment, reactor was purged with nitrogen gas at 94°C for about 1.5 h to ensure the absence of moisture and oxygen. After cooling the reactor to 83°C, it was fed with 500 mL of dry heptane, and then, with stirring, a given Al/Ti molar ratio of TEAL, halocarbon and catalyst were added by means of syringe in an atmosphere of purified nitrogen. The reactor was pressurized with 5 bar hydrogen, and then ethylene was fed to maintain a reactor pressure of 8.5 bar, the temperature was controlled at 83°C, and stirrer speed was 500 rpm to minimize ethylene transport limitations. Residence time was kept constant at 1 h, and at the end, the reactor was discharged and the powder polymer was dried in air.

RESULTS AND DISCUSSION

In the previous study, chlorocyclohexane (CHC), chlorocyclopentane (CHP), butylchloride (BC), 1,4-dichlorobutane (DCB), and chloroform (C) were tested as promoters for a Titanium-based Ziegler-Natta catalyst in the slurry phase ethylene polymerization.[10] We found out that with increasing the ratio of halocarbon/titanium, the activity has a peak value and the peak value changes greatly for different promoters. Similar observation has been reported earlier in the case of ethylene copolymerization using Ziegler-Natta catalyst.[11] For our system (without H_2), halocarbon/titanium optimum amounts were 128, 110, 20, 0.54, and 0.033 for CHC, CHP, BC, DCB, and C, respectively.

On the other hand, hydrogen is the most widely used chain-transfer agent for molecular weight control with Ziegler-Natta systems in industry. It is the only commercially applicable chain-transfer agent in the low-pressure olefin polymerization process over the Ziegler-Natta catalysts and is commonly used to adjust the molecular weight and thereby the processability of the material. In this article, promoting effect of halocarbons was studied by using H_2 as chain transfer agent under the conditions of H_2/C_2H_4 = 5/3.5 bar at optimum amount of HC/Ti molar ratios that were found in the previous paper for systems without H_2. Also, the effect of halocarbons on the some properties of the obtained polymers including particle size distribution, bulk density, melt flow index (MFI), thermal properties, and wax amount were studied.

Polymerization results from a series of experiments with several different potential promoters were shown in Table I both in the presence and absence of H_2. Hydrogen which is used to control the polymer molecular weight is believed to decrease catalyst reactivity.[12] Results in Table I indicate that when no HC is used, H_2 decreased catalyst activity from 16.88 to 10.50 KgPE/gr Cat.hr, which could be related to inhibition effect of H_2 at lower partial pressure of ethylene. However, activity improvement effect of halocarbons in the presence of H_2 is more than that for the systems without H_2, except for DCB, so that, one can conclude that the inhibition effect of H_2 in ethylene polymerization changes when HC is present in the polymerization system.

Rate of polymerization (R_p) was studied in more detail for the more efficient promoter, i.e., chlorocyclohexane. The effect of CHC on the R_p during the polymerization time was illustrated in Figure 1. As can be seen, in both cases (with and without CHC), after 3–4 min catalyst activity reached to a maximum peak value and then decreased with time, therefore, it is concluded that R_p trend has not been changed. However, in the presence of CHC, rate of ethylene consumption was higher than that in blank system.
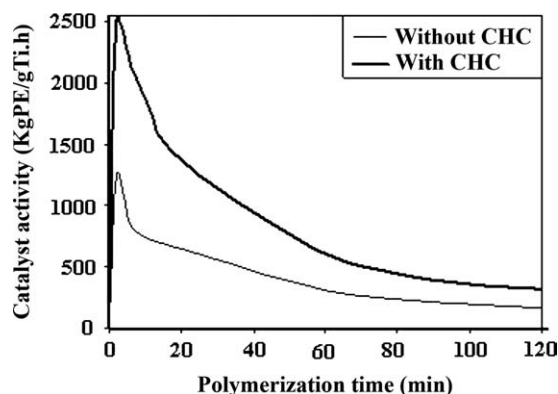
Figure 1 Effect of chlorocyclohexane on the R_p (catalyst activity) during the polymerization time; polymerization conditions are: CHC/Ti: 0 (without halocarbon) and 128, P: 8.5 bar, T: 83°C, Al/Ti = 180, t: 2 h.

MFI

A good indication of the processability of a polymer can be obtained from measurements of the melt flow index and melt flow ratio. The obtained polymers were characterized by MFI analysis (Table II). Results showed that in the presence of halocarbons, MFI was increased as compared with systems without halocarbon. It is concluded that, in systems containing halocarbons, the rate of chain-transfer reaction increases, resulting in the increase of MFI. Thus, these systems have a better hydrogen response than the systems without halocarbons, and therefore, in the presence of halocarbons lesser amount of H_2 has been needed to reach a certain MFI. So, another advantage of halocarbons could be the decrease of activity depression that is resulted from applying H_2 in the polymerization system. Considering the results of MFI analysis; it is possible to control MFI of polymer by applying halocarbons as promoter.

On the other hand, MFR is an indication of the polymer molecular weight distribution. MFR results from Table II showed that halocarbons broadened MFRs and consequently molecular weight distributions. Polymers with broader molecular weight distributions have better processability than polymers with narrower distributions. So, it is supposed that
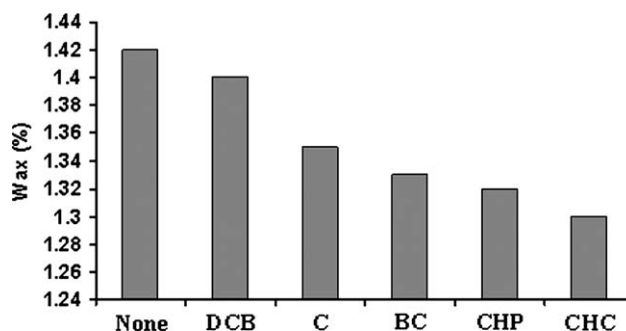

Figure 2 Effect of different halocarbons on wax amount of produced polyethylenes, polymerization conditions are: P: 8.5 bar, T: 83°C, t: 1 h, Al/Ti = 180, H_2 = 5 bar.

by using halocarbons, PEs with improved processability have been obtained.

WAX

The content of soluble part of the produced polymers was measured by means of Soxhlet extraction technique.[1] This content was expressed in weight percentage (Fig. 2 and Table II). Results from Table II clearly showed that halocarbons have a good effect in decreasing wax amount of the polymer. In the laboratory scale this effect may not be very significant, but in industrial scale this effect can be significant.

This result is in agreement with Koch's result, who introduced halocarbons as byproduct suppressors.[6] Among different promoters, CHC has the greatest effect in decreasing wax amount of the produced polymer.

Decrease in wax amount could be related to two phenomena: (a) deactivation of active species producing low MW oligomer/polymer; (b) increase of catalyst life time. During polymerization, loss of Cl from the active species can lead to reduction and deactivation. In that situation, reoxidation of Ti by a halocarbon may restore the active species, leading to increased catalyst stability and longer catalyst life time.

TABLE II
Effect of halocarbons on MFI, MFR, and WAX Amount of Produced Polymers

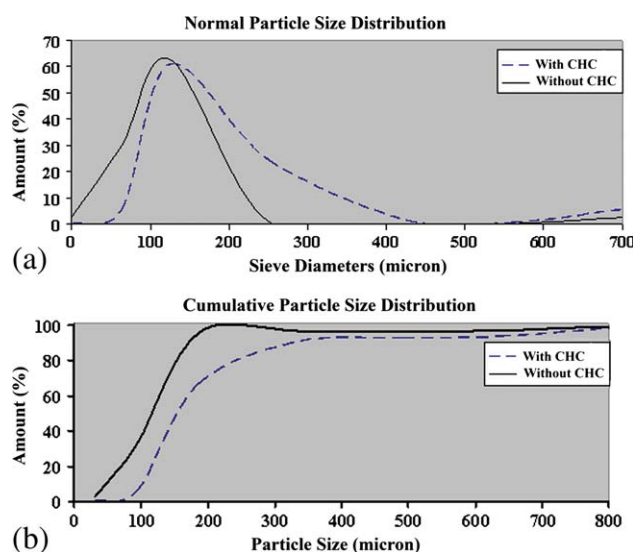| Halocarbon Type	MFI_2 (gr PE/10 min) (2.16 Kg, 190°C)	MFI_{10} (gr PE/10 min) (10 Kg, 190°C)	MFR	Wax Amount (%)
Without promoter	0.40	10.58	26.45	1.42
Chlorocyclohexane	0.48	17.2	35.83	1.30
Chlorocyclopentane	0.45	14.8	32.89	1.32
Butylchloride	0.45	13.4	29.78	1.33
1,4-Dichlorobutane	0.47	14.7	31.28	1.4
Chloroform	0.44	15.3	34.77	1.35

Figure 3 Effect of CHC on (a) Normal Particle Size Distribution; and (b) Cumulative Particle Size Distributions of produced PE. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PSD

During the ethylene polymerization, fine polymer particles will likely cause the generation of static electricity, the occurrence of "dust" phenomenon, and sometimes the formation of agglomerates which might block the transfer conduit systems. In several industrial applications, knowledge of the particle size and PSD span is critical for controlling and improving product quality and handling. To measure PSD of the polymers, sieve analysis has been employed.

Normal and cumulative curve of particle size distribution for catalyst system without halocarbon and system containing CHC were shown in Figure 3(a,b), respectively. In probability theory and statistics, the normal distribution or Gaussian distribution is a continuous probability distribution that describes data which clusters around a mean or average. The graph of the associated probability density function

is bell-shaped, with a peak at the mean, and is known as the Gaussian function or bell curve. The normal distribution can be used to describe, at least approximately, any variable that tends to cluster around the mean. As shown in Figure 3(a), in the presence of CHC, particle size of PE shifted to the higher amounts. Datas from PSD analysis were collected in Table III. As shown, average particle size of PE obtained from catalyst system was increased from 123 micron to 197, 192, 188, 154, and 180 micron for system containing CHC, CHP, BC, DCB, and C, respectively.

On the other hand, the cumulative distribution function of a probability distribution, evaluated at a number x, is the probability of the event that a random variable X with that distribution is less than or equal to x. $d_{0.1}$, $d_{0.5}$, and $d_{0.9}$ which are good criteria to measure polymer particle size have been derived from cumulative distribution curve. As shown in Table III, in the presence of halocarbons, $d_{0.1}$, $d_{0.5}$, and $d_{0.9}$ of PEs were increased, and CHC had the maximum effect on increasing particle size. Cumulative distribution of particle size for PEs obtained from catalyst system without CHC and system containing CHC was shown in Figure 3(b).

Also, the PSD span of the product was increased from 1.05 to 1.44, 1.43, 1.39, 1.40, and 1.42 for system containing CHC, CHP, BC, DCB, and C, respectively.

Particle size can have influence on the bulk density of the polymers. The increases in bulk density in Table III are consistent with the increases in particle size and the broader particle size distribution.

Thermal properties

To determine the effect of halocarbons on T_m and crystallinity of the polymers, DSC analysis has been employed and results obtained were presented in Table IV.

DSC curves for all polyethylene samples show a single and relatively broad melting peak indicating

TABLE III
Effect of Halocarbons on Particle Size, PSD Span, and Bulk Density of Polyethylenes

Halocarbon type	Average particle size (micron)	$d_{0.1}$ (micron)	$d_{0.5}$ (micron)	$d_{0.9}$ (micron)	PSD span[a]	Bulk density (g/cm^3)
Without promoter	123	48	117	171	1.05	0.35
Chlorocyclohexane	197	102	155	325	1.44	0.38
Chlorocyclopentane	192	96	153	315	1.43	0.38
Butylchloride	188	84	147	288	1.39	0.37
1,4-Dichlorobutane	154	61	129	241	1.40	0.36
Chloroform	180	78	144	282	1.42	0.36

$d_{0.1}$, $d_{0.5}$, and $d_{0.9}$ mean that 10, 50, and 90% of the particles have less than or equal to the corresponding indicated particle diameter (μm), respectively. PSD: particle size distribution.
[a] $[d_{0.9} - d_{0.1}]/d_{0.5}$.

no appreciable molecular reorganization during the heat treatment. Figure 4(a,b) show the DSC diagram of samples without and with CHC, respectively.

The thermal properties between the nascent powders (1st heating) and the melt-crystallized samples (2 nd heating) of these polyethylenes were the same and the melting temperature did not change significantly in the first and second heating, and the values were found in the region commonly for HDPE.[13]

The degree of crystallinity of semicrystalline polymers has considerable effect on their mechanical and thermal properties. The effect of halocarbons on the polymer crystallinity as determined by ΔH (J/g) was calculated by the division of the observed heat of fusion by 288 J/g and shown in Table IV. For the 1st heating run, crystallinity of PEs was increased from 63.96% for catalyst system without halocarbon to maximum amount of 69.55% for catalyst system containing CHC as promoter. The increases in DSC crystallinity of the polyethylenes obtained can be attributed to the broadening in molecular weight distribution, apparent from the data in Table II.

On the other hand, for 2nd run this increase was from 68.5 to 74.23. In all cases, the crystallinities of the melt-crystallized samples were higher than nascent powders. Crystallinity data showed that, in the presence of halocarbons crystallinity of PEs was increased; therefore, halocarbon promoters could have good effect on improving mechanical properties of PEs. Among studied halocarbons, CHC had the most effect on increasing crystallinity of PEs.

CONCLUSIONS

The association of some halocarbon compounds including chlorocyclohexane (CHC), chlorocyclopentane (CHP), butylchloride (BC), 1,4-dichlorobutane (DCB), and chloroform (C) with the $MgCl_2$ (Ethoxide type)/$TiCl_4$/$AlEt_3$/H_2 catalytic system was studied. The results of the present work were summarized as follows:
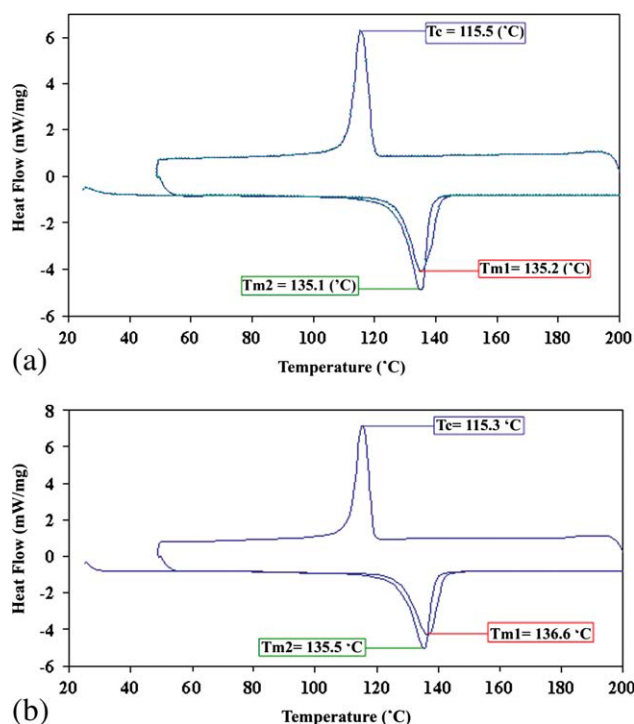

Figure 4 DSC curves of PEs prepared via catalyst system (a) without CHC; (b) with CHC (CHC/Ti = 128). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

1. Halocarbons increased catalyst activity by 66–95%, depending on the nature of the halocarbon.
2. Results from melt flow test showed that in the presence of halocarbons, MFI was increased and MFR broadened as compared with systems without halocarbon. So, it is concluded that by using halocarbons, PEs with improved processability have been obtained.
3. Halocarbons had a great effect in decreasing wax amount of the polymer and among them, CHC had the most effect.
4. Melting temperature of the PEs did not change significantly, and the values were founded in the region commonly for HDPE.
5. Crystallinity data showed that, in the presence of halocarbons crystallinity of PEs was increased. Among studied halocarbons, CHC had the most effect on improving crystallinity of PEs.
6. Halocarbons increased particle size, PSD span and bulk density of the polymers.

So, the association of studied halocarbon compounds with Titanium-based Ziegler-Natta catalyst could be a potential alternative way to increase more its catalytic performances.

TABLE IV
Effect of halocarbons on Melt Temperature and Crystallinity of polyethylenes

Halocarbon Type	T_{m1} (°C)	T_{m2} (°C)	X_{C1} (%)	X_{C2} (%)
Without promoter	135.2	135.1	63.95	68.5
Chlorocyclohexane	136.6	135.5	69.55	74.23
Chlorocyclopentane	136.4	135.2	67.68	69.80
Butylchloride	135.7	135.3	64.73	68.70
1,4-Dichlorobutane	135.3	135.2	64.89	70.17
Chloroform	136.1	135.4	67.25	72.43

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