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European Polymer Journal 43 (2007) 3688–3694

EUROPEAN POLYMER JOURNAL

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Short communication

# Biphasic ethylene polymerisation using ionic liquid over a titanocene catalyst activated by an alkyl aluminium compound

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Received 2 March 2007; received in revised form 13 May 2007; accepted 14 May 2007
Available online 2 June 2007

## Abstract

1-*n*-Butyl-3-methylimidazolium tetrachloroaluminate ($[BMIM]^+[AlCl_4]^-$) was applied to biphasic ionic liquid/hexane ethylene polymerisation as a medium of the $Cp_2TiCl_2$ titanocene catalyst activated by alkylaluminium compounds (MAO, $AlEt_2Cl$, $AlEt_3$). The best results were obtained using $AlEt_2Cl$. The results show that catalyst recycling, higher ethylene pressure, and greater Al/Ti molar ratio along with a greater volume of the ionic liquid phase enhance catalyst activity. The polyethylene gathered from the hexane phase is characterised primarily by its high purity. Its physical properties remain polyethylene obtained over a heterogeneous metallocene catalyst. Thus, biphasic ionic liquid polymerisation using a metallocene catalyst is possible and offers interesting technological implications.

*Keywords:* Ethylene polymerisation; Ionic liquid; Metallocene catalyst; Biphasic process

## 1. Introduction

Since the discovery of metallocene catalysts for olefin polymerisation, there have been continuous efforts to apply them in industrial processes. The typical way of modification is heterogenisation of the metallocene catalysts on a solid carrier, which is a prerequisite to enable them to be applied in continuous operation in the slurry, bulk-monomer, or gas-phase processes [1–3].

Recently, due to their polar but weakly coordinating character, ionic liquids have attracted considerable interest as solvents for many catalytic reactions [4–10]. Amongst the many examples of polymerisation reactions carried out in an ionic liquid medium, hardly any concern non-functionalised α-olefins. In the case of early transition metals, there are two reports concerning the polymerisation of ethylene [11,12]. The polymerisation was performed in 1-ethyl-3-methylimidazolium tetrachloroaluminate acidic ionic liquid over the Ziegler–Natta $TiCl_4$ catalyst activated by $AlEtCl_2$ and the metallocene $Cp_2TiCl_2$ catalyst activated $Al_2Me_3Cl_3$. The $Cp_2ZrCl_2$ and $Cp_2HfCl_2$ catalysts were discovered to be inactive in the same conditions. The studies

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doi:10.1016/j.eurpolymj.2007.05.034

were not continued and there is scarce data about the physical properties of the polyethylene obtained. Promising results were obtained in the case of late-metal catalysts where (1,4-bis(2,6-diisopropylphenyl)acenaphthenediimine)dichloronickel(II) was applied to ethylene polymerisation in 1-*n*-butyl-3-methylimidazolium organochloroaluminate ionic liquid. The reaction proceeds as a typical biphasic system where the nickel catalyst is immobilized in the ionic liquid and the products in the organic phase (toluene). The ionic catalyst solution could be reused in successive polymerisation cycles upon the addition of an alkylaluminium cocatalyst [13]. Similarly, ionic liquids have been successfully applied as a medium for cationic Ni-complexes in biphasic oligomerisation of ethylene to α-olefin [14,15].

Ionic liquids, non-volatile and immiscible with numerous organic solvents, seem to be excellent for non-aqueous polar biphasic catalytic reactions. The product separation can be easily obtained by simple decantation. The catalyst maintained in the ionic liquid can be reused (recycled). All this together indicates that the application of metallocene catalysts in biphasic processes using ionic liquid is a potential alternative to their heterogenisation on a solid carrier.

This works describes how the $Cp_2TiCl_2$ catalyst activated by alkylaluminium compounds behaves in the biphasic process of ethylene polymerisation using 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate $[BMIM]^+[AlCl_4]^-$ ionic liquid. The properties of the polyethylene obtained are also presented.

## 2. Experimental part

### 2.1. Materials

Ethylene (Linde AG Gaz) and pure nitrogen (Polgaz) were used after having been passed through a column of sodium metal supported on $Al_2O_3$. Pure-grade hexane (POCH, Gliwice) was refined with sulfuric acid, dried by refluxing in argon from the sodium metal, and stored over 4A molecular sieves. Bis(cyclopentadienyl)titanium(IV) dichloride – $Cp_2TiCl_2$ (Aldrich), methylaluminoxane – MAO (10 wt.% as toluene solution, Aldrich), triethylaluminium – $AlEt_3$, and diethylaluminium chloride – $AlEt_2Cl$ (1 M as hexane solution Aldrich), ionic liquid $[BMIM]^+[AlCl_4]^-$ – 1-*n*-butyl-3-methylimidazolium tetrachloroaluminate (Aldrich, assay $\geqslant$95 wt.%), HCl 35–38 wt.%, $H_2SO_4$ 98 wt.%, and HF 40 wt.% (POCH, Gliwice) were applied as purchased. 1,2,4-Trichlorobenzene – TCB (99 wt.%) (Aldrich) was purified by distillation.

### 2.2. Instruments

The FT-IR analysis was accomplished using a Philips Analytical PU 9800 spectrometer, Resolution $R = 2\ cm^{-1}$, Bands 4000–400 $cm^{-1}$, in Nujol KBr/KBr. The molecular weight and molecular weight distribution of each polymer sample was determined by gel permeation chromatography (GPC, Waters 150-CV) using 1,2,4-trichlorobenzene as the solvent at 142 °C. The data were analysed using polystyrene calibration curves. The degree of crystallinity and the melting temperature of the polyethylene were estimated with a DSC 2010 TA Instruments Differential Scanning Calorimeter. The polymer crystallinity was calculated using the equation: $C = (\Delta h_f/\Delta h_{t,c}) \times 100\%$ where; $\Delta h_f$ is the heat of fusion of the polyethylene sample, $\Delta h_{f,c}$ is the heat of fusion of standard, $C$ is the crystallinity, %.

The linearity of the polyethylene was analysed using a Nicole Nexus 2002 FT-IR spectrometer. The samples, in the form of tablets, consisted of the polyethylene powder and KBr. The number of branches in the polyethylene was estimated on the basis of the ratio of the band at 1379.3 $cm^{-1}$ to the band at 1368.7 $cm^{-1}$. The former band results mainly from the presence of terminal methyl groups on the branches. The latter is the band of absorption of the methylene groups. Additionally, $^{13}C$ nuclear magnetic resonance spectra were recorded on a Bruker Ultrashield spectrometer (400 MHz). The polyethylene samples were dissolved in 1,2,4-trichlorobenzene at 150 °C for minutes before being run at 130 °C. The single signals at ~29.3 ppm indicated the linear structure of the polyethylenes.

### 2.3. Ethylene polymerisation

All steps were carried out in oxygen-free conditions using an inert nitrogen atmosphere. The alkylaluminium compound (MAO, $AlEt_2Cl$, $AlEt_3$) was added both to the ionic liquid and the hexane phases to act not only as an activator but also as a scavenger of impurities. The alkylaluminium compound was added at the ionic liquid/alkylaluminium compound molar ratio 10/1. The mixture was left to