Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer Degradation and Stability 90 (2005) 264–271
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

Poly(vinyl alcohol) obtained by hydrolysis of poly(vinyl silyl ethers) and poly(vinyl ethers) synthesized with indenyltitanium trichloride

Isidro Palos, Gregorio Cadenas-Pliego*, Sergei Ya. Knjazhanski, Enrique J. Jiménez-Regalado, Edgar G. De Casas, V.H. Ponce-Ibarra

Centro de Investigación en Química Aplicada (CIQA), Boulevard Enrique Reyna No 140 Saltillo, 25100 Coahuila, México

Received 18 November 2004; received in revised form 3 March 2005; accepted 17 March 2005
Available online 15 July 2005

Abstract

Vinyl ether and vinyl silyl ether (VSiE) monomers were polymerized in methylene chloride with an indenyltitanium trichloride catalyst using methyl aluminoxane as co-catalyst. The polymerization reactions were carried out at different temperatures and using an [MAO]/[IndTiCl$_3$] = 10 molar ratio. The stereoregularity of the polymers was determined by NMR analysis. The molecular weights (M_n's) observed in the polymers obtained from vinyl silyl ethers were lower than the respective poly vinyl ethers. The polymer hydrolysis reactions produced PVA's with the same stereoregularity, the tacticities of new the PVA's were different compared with the PVA produced by the traditional reaction of poly(vinyl acetate) hydrolysis. The most important syndiotacticity (rr) observed in the products obtained from the VSiE polymerization reaction was in the range of 28–39%, while the heterotactic fractions (mr) observed in the PVA's produced from the specific poly(vinyl dimethylphenylsilyl ether) and poly(*tert*-butyl vinyl ether) hydrolysis reactions were 52 and 57%, respectively.

Keywords: Stereospecific polymerization; Metallocene catalyst; Syndiotactic PVA; Heterotactic PVA; Poly(vinyl ethers)

1. Introduction

During the last decades, the polymerization of vinyl acetate (PVAc), as well as of different poly(vinyl esters) and poly(vinyl ethers) (PVE), has been studied with more interest [1–3]. The reason is because those polymers are precursors of poly(vinyl alcohol) (PVA). This polymer has a great number of applications; for example, it can be employed in some polymerizations as a stabilizer and also contributes to the emulsification of water colloidal dispersions. The PVA is also used for its excellent oxygen barrier property in food and medicine industries. The molecular weight and the hydrolysis degree directly affect the properties of the polymer, when reducing the hydrolysis degree and/or the molecular weight, the flexibility increases, as well as the affinity for water and adhesion to hydrophobic surfaces. On the other hand, if such properties increase, the viscosity, impact resistance, as well as resistance to organic solvents such as gasoline, benzene and xylene increase among others [4].

The commercial PVA available is generally obtained by hydrolysis (saponification) of poly(vinyl acetate) synthesized by free radical polymerization and has a syndiotactic fraction (*r* diads) of 52–54%. Polymerizations of bulky vinyl esters, such as vinyl trifluoroacetate, vinyl pivalate, vinyl diphenylacetate and vinyl 2,2-bis(trifluoromethyl) propionate are known

* Corresponding author. Tel.: +52 844 438 98 30.
E-mail address: gpliego@ciqa.mx (G. Cadenas-Pliego).

0141-3910/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2005.03.020

to produce polymers rich in syndiotacticity, which can be converted to PVA [5]. The saponification of polymers obtained from vinyl ester polymerization in fluoroalcohols as solvents, produces a PVA with $r = 69-72\%$ [6]. Vinyl ethers (VE) and vinyl silyl ethers (VSiE), such as benzyl vinyl ether, *tert*-butyl vinyl ether and vinyl trimethylsilyl ether have been also studied as starting monomers to obtain stereoregular PVAs. Ohgi and Sato carried out the polymerization of vinyl ethers, obtaining an isotactic PVA derived from poly *tert*-butyl vinyl ether polymerized with $BF_3 \cdot OEt_2$ catalyst and others derivatives, using toluene as solvent at −78 °C. The hydrolysis was made with HBr at 0 °C in methylene chloride or toluene [7].

With the purpose of enhancing the properties of the polymers and to design them with certain structural order, new catalysts arose, making it possible to produce polymers with different tacticity. The first such catalysts used were the Ziegler–Natta catalysts, which have stayed dominant until arrival to what we know as metallocene catalysts. The metallocene catalysts made possible the synthesis of isotactic and syndiotactic polypropylene [8,9], as well as syndiotactic polystyrene [10]; besides achieving an order in the structure, it is also possible to control the molecular weight in the polymer [11,12].

Baird and co-workers [13] studied vinyl ether (VE) polymerization with the $Cp^*TiMe_3/B(C_6F_5)_3$ [$Cp^* = \eta^5$-pentamethylcyclopentadienyl] catalytic system. The complex formed was very active and versatile with other polar monomers, such as *N*-vinyl carbazole; in particular, *iso*-butyl vinyl ether (IBVE) polymerization reaction proceeded instantaneously at room temperature, while at −78 °C it was carried out in a few minutes. The polymerization in CH_2Cl_2 at −78 °C produces a poly(*iso*-butyl vinyl ether) (PIBVE) with $M_n = 4.1 \times 10^{-4}$ g/mol and relatively high polydispersity ($M_w/M_n = 2.4$); the polymer produced contained a syndiotactic fraction of 56% and an isotactic fraction of 44%.

In this work, the hydrolysis of some poly(vinyl silyl ethers) and poly(vinyl ethers), obtained by means of polymerization with a metallocene catalyst, is reported; with the aim of obtaining a new method to produce PVA with a higher syndiotacticity than that produced by the traditional poly(vinyl acetate) hydrolysis (Fig. 1).

2. Experimental

All the synthesis, polymerization and hydrolysis reactions were carried out in inert atmosphere using the Schlenk technique; the monomers were synthesized in the laboratory according to reported methods [14]. The indenyltitanium trichloride ($IndTiCl_3$) was synthesized in the laboratory according to literature methods [15]. The monomers used for the polymerizations were vinyl diethylisopropylsilyl ether (VDEISi), vinyl dimethylphenylsilyl ether (VDMPSiE), *iso*-butyl vinyl ether (IBVE) and *tert*-butyl vinyl ether(*t*BVe). The vinyl silyl ethers were synthesized in the laboratory and the vinyl ethers were obtained from Aldrich. The vinyl ethers were purified by distillation from CaH_2 under inert atmosphere, before their use. The methyl aluminoxane (MAO) solution, from Aldrich, was purified by evacuating the solvent (toluene) in vacuum at 50 °C and then adding dried toluene purified in the laboratory.

2.1. Polymerization reactions

The IBVE polymerization was carried out with ratios of [monomer]/[catalyst] = 400 and [MAO]/[catalyst] = 10 (mol/mol). The ratios for the vinyl silyl ethers were [monomer]/[catalyst] = 196 and [MAO]/[catalyst] = 10 (mol/mol) and for the *tert*-butyl vinyl ether were [monomer]/[catalyst] = 180 and [MAO]/[catalyst] = 10 (mol/mol), the amount of catalyst was 60 mg (2.22×10^{-4} mol) for all the polymerization reactions.

The first step of the followed methodology was the addition of 35 mL of solvent (toluene for the vinyl silyl ethers or methylene chloride for vinyl ethers) and the monomer in a Schlenk flask. In a separate flask, the catalytic system was prepared with 60 mg of the catalyst indenyltitanium trichloride (dissolved in methylene chloride) and 1.8 mL of the MAO solution (1.23 M). Once the activation of the catalytic system was completed (4 min), the content was added to the flask with solvent and monomer previously conditioned to the reaction temperature. Once the reaction time was reached, in the vinyl silyl ethers polymerization, a small amount of methanol was added and immediately the solvent of the reaction flask extracted, to finally dry the product and analyze it by means of ^1H and ^{13}C NMR, as well as by GPC for molecular weight determination. In the case of the vinyl ether polymerizations, the reaction was stopped by adding 2 mL of methanol/HCl 10% solution and then the product precipitated in methanol.

2.2. Hydrolysis of poly(vinyl silyl ethers) and poly(vinyl ethers)

The obtained polymer was dissolved in 35 mL of toluene and HBr gas was passed in a [polymer]:[HBr] = 1:2 mol ratio for the hydrolysis reaction. The HBr gas was introduced into the reaction flask by means of a manifold system. Such reaction was carried out at 0 °C temperature for around 30 min, the precipitate was collected and washed with methanol