COPOLYMERIZATION OF PROPENE AND STYRENE USING A ZIRCONOCENE – METHYLALUMINOXANE INITIATOR SYSTEM

F. M. Rabagliati,1* F. J. Rodríguez,1§ R. Quijada,2 and G. B. Galland3

1 Grupo de Polímeros, Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile. Casilla 40, Correo 33, Santiago, Chile. E.mail: franco.rabagliati@usach.cl
2 Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 2777, Santiago, Chile.

The copolymerization of propene with styrene has been tested using the rac-Et(Ind)2ZrCl2-methylaluminoxane (MAO) initiator system. The various proportion of styrene in initial feed showed an important effect on the polymerization activity. Low contents of styrene in the reaction produced a considerable fall in the activity. Respect to thermal behavior, it is noted that obtained propene/styrene copolymers showed Tm values slightly lower than the corresponding polypropene one. NMR spectroscopy allowed to confirm that the copolymer composition includes a very low incorporation of styrene in polypropylene chains.

Keywords: Metallocene – Propene – Styrene – Coordination Polymerization

Introduction

In last decades, the metallocene – methylaluminoxane initiator systems have been largely utilized in the polymerization of vinyl monomers. In contrast with the traditional Ziegler – Natta catalysts, the metallocenic systems are characterized to allow a better control of the microstructure and of the molecular weight. One type of active site (single site) and easily modifiable structures of metallocenes have characterized to these novel systems[1].

Polyethylene and polypropylene are polymeric materials demanded worldwide. According to information of the Plastics Division of the American Chemistry Council, in 2007 the production of these polyolefins reached an important 64% of the total production of thermoplastics in North America[2]. Their polymerizations initiated by metallocene-MAO systems have been widely studied. Control of activity, microstructure and molecular weight have characterized these homogeneous systems. These systems have also been used to study diverse copolymerizations. Monomer and metallocene structure, temperature, MAO concentration, among others, have been determinant to obtain a copolymer.

In previous works we have reported on diverse copolymerization studies using metallocene-MAO initiator systems. Ethylene/α-olefins[3-5], ethylene/dicyclopentadiene[6], styrene/substituted styrene[7-9], styrene/α-olefins[10] copolymers, among others, have been obtained.

§ Present address: Laboratorio de Envases (LABEN-CHILE). Departamento de Ciencia y Tecnología de Alimentos. Facultad Tecnológica. Universidad de Santiago de Chile. Obispo Manuel Umaña 050, Estación Central, Santiago Chile.
The present study reports the results obtained in propene/styrene copolymerization using a zirconocene-MAO initiator system.

**Experimental**

1. **Materials.**

The solvent (toluene, J.T.Baker) was purified by refluxing over metallic sodium, with benzophenone as indicator. Styrene (Aldrich, ≥ 99%) was purified by means washing with a NaOH solution (5%), dried over CaH₂ and distilled under reduced pressure. Polymerization grade propene (Petroquim S.A) was deoxygenated in a column containing BASF R3-11 catalyst, and then dried by passing it through a column of 4Å molecular sieves. The methylaluminoxane (Witco) and rac-Et(Ind)₂ZrCl₂ (Boulder Scientific Company) were used without prior treatment. All operations were carried out in an atmosphere of high purity N₂ (99,95%), using a dry box and the Schlenk technique for handling the zirconocene and MAO solutions.

2. **Polymerization.**

Homo- and copolymerizations were carried out in a 1-liter Büchi glass reactor. The required volumes of toluene, MAO solution and styrene were charged sequentially by syringe under nitrogen pressure. As soon as the nitrogen of the reactor was evacuated, the propene was incorporated to reach the required pressure (2 bar). Polymerization was initiated by injection of metallocene solution. The reactions were kept at 60°C under stirring (1000 rpm) for 30 min and terminated by addition of a methanol acidified solution (HCl, 2%). The polymer was recovered by filtration, washed repeatedly with methanol and dried at room temperature. Finally, the copolymerization products were extracted with acetone for 4 hours.

3. **Characterization.**

3.1 **Thermal analysis.** Differential Scanning Calorimetry (DSC) analyses were conducted with a Mettler DSC-822 calorimeter. 5-6 mg samples were heated at a rate of 20 °C min⁻¹ from -50 °C to 200 °C under nitrogen atmosphere. The report Tg and Tm were those obtained in the second heating scan.

3.2 **Molecular Weights.** Molecular weights were determined by GPC in a Waters Alliance 2000 GPC system equipped with an optic differential refractometer. Three separation columns, HT6E, HT5 and HT3 were used, previously calibrated with narrow molecular weight distribution polystyrene standards. 1,2,4-Trichlorobenzene was used as solvent and a flow rate of 1 mL min⁻¹ at 135°C.
3.3 Nuclear Magnetic Resonance. The $^{13}$C and $^1$H-NMR and spectra were obtained at 80°C on a Varian Inova 300 spectrometer operating at 75 and at 300 MHz, respectively. The samples were prepared by dissolving the polymer in 1,1,2,2-tetrachloroethane-$d_2$ in 5 mm sample tubes. The chemical shift was referenced to TMS. The spectra were taken with a flip angle of 74°, an acquisition time of 1.5 s and a decay time of 4.0 s.

Results and Discussion

Table 1 shows the results of propene/styrene copolymerization using rac-Et(Ind)$_2$ZrCl$_2$ – MAO system. It is possible to observe an important effect of styrene content, at initial feed, on the polymerization activity and on molecular weights of resulting copolymers. Low content of styrene in the feed cause a significant decrease in initiator activity, while molecular weights are reduced gradually. Soga et al. [11] working with the catalyst system composed of Solvay Type TiCl$_3$ and metallocene Cp$_2$TiCl$_2$ reported reactivity ratios of $r_{\text{propene}} = 130$ and $r_{\text{styrene}} = 0.18$. On the other hand, the thermal behavior of obtained copolymerization products showed a slight effect on Tm with the increase of styrene in the feed (Figure 1). Similar situation we observed when copolymerizing styrene with α-methylstyrene where also a low incorporation of comonomer was reached accordingly to $^{13}$C-NMR analysis.[7] In our cases the aromatic styrene signal at low field tells about the presence of styrene units along the main polypropene chains. Furthermore these results are in agreement with Talapatra et al. who reported low styrene incorporation when performing propene-styrene copolymerization with Ziegler-Natta catalysts[12].

Table 1. Propene/styrene copolymerization using Et(Ind)$_2$ZrCl$_2$-MAO initiator system in toluene at 60 °C for 30 minutes.

<table>
<thead>
<tr>
<th>[Styrene]$_0$ (mol/L)$^a$</th>
<th>Product Weight (g)</th>
<th>Activity$^b$</th>
<th>Tm (°C)</th>
<th>Mw $\times 10^{-4}$ (g/mol)</th>
<th>Mw/Mn</th>
<th>Styrene content in copolymer (% mol)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>64.0</td>
<td>12749</td>
<td>123</td>
<td>1.7</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>0.017</td>
<td>48.3</td>
<td>9622</td>
<td>119</td>
<td>1.4</td>
<td>1.6</td>
<td>0.02</td>
</tr>
<tr>
<td>0.035</td>
<td>23.8</td>
<td>4741</td>
<td>119</td>
<td>1.2</td>
<td>1.5</td>
<td>nd</td>
</tr>
<tr>
<td>0.052</td>
<td>20.9</td>
<td>4163</td>
<td>118</td>
<td>1.0</td>
<td>1.4</td>
<td>nd</td>
</tr>
<tr>
<td>0.070</td>
<td>15.3</td>
<td>3048</td>
<td>117</td>
<td>0.9</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>0.087</td>
<td>8.8</td>
<td>1753</td>
<td>117</td>
<td>0.7</td>
<td>1.4</td>
<td>nd</td>
</tr>
<tr>
<td>0.105</td>
<td>6.9</td>
<td>1375</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>0.6</td>
</tr>
<tr>
<td>0.209</td>
<td>traces</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ In the initial feed
$^b$ Defined by Kg Polymer/(mol Zr x time (h) x pressure (bar))
$^c$ Determined by NMR $^1$H
Figure 1. - DSC thermograms for Propene/Styrene copolymers obtained using 
$\text{Et(Ind)}_2\text{ZrCl}_2$-MAO initiator system at various initial S contents

Figure 2. - $^1\text{H}$-NMR and $^{13}\text{C}$-NMR spectra of copolymer propene/estyrene (initial feed: 0.035 mol/L styrene) 
obtained using $\text{Et(Ind)}_2\text{ZrCl}_2$-MAO initiator system

Figure 2 shows $^1\text{H}$- and $^{13}\text{C}$-NMR spectra of obtained product when polymerizing 
propene/styrene mixture at initial feed of 0.035 mol/L of styrene. In (A), $^1\text{H}$-NMR spectrum, 
signals at 7 – 7.2 ppm, show the H-aromatics of styrene-benzene ring. Spectrum (B), $^{13}\text{C}$-NMR ,
shows the peaks of styrene at 121, 129 (two peaks) and at 143 ppm the quaternary-C signal. 
The very small signals at 112 ppm, are attributable to olefin terminal. The other peaks in the aliphatic 
region, non corresponding to propene units, can be assigned to aliphatic terminal groups and, maybe 
some of them, from PS sequences. Peaks near 73 ppm are due to solvent.
As it can be seen in Figure 1, Tm values slightly diminish as increase styrene content at copolymer. The low incorporation of styrene it is in accordance with a much lower reactivity of styrene when compared with propene. Accordingly with values of reactivity ratios determined by Soga et al.[11] for propene and styrene, when copolymerized using Cp₂TiCl₂ combined with Solvay Type TiCl₃ initiator system. Anyhow, they employed a titanocene instead of a zirconocene in their polymerization process.

This effect it can also be noted in front of molecular weights of the obtained copolymers (Table 1). As styrene units incorporate at propagating copolymer chains, the coordination and incorporation of propene units become more difficult, and shorter chains (lower molecular weight) are produced.

Conclusions

Et(Ind)₂ZrCl₂ – MAO initiator system induce the copolymerization of propene with styrene with low incorporation of styrene units. Results indicate that polymerization activity, molecular weights of obtained copolymers and their thermal behavior depend on propene/styrene content in the initial feed. Copolymerization activities diminish with increase of styrene content at initial feed. The copolymer obtained showed narrow MWD in accordance with polymerizations catalyzed by metallocenes.

Acknowledgements

Financial support from Fondo Nacional de Desarrollo Científico y Tecnológico, FONDECYT, Grant 1085061, is gratefully acknowledged. To Laben Chile (USACH) for DSC measurements.

References

11. Soga K, Yanagihara H. Macromecules 1989, 22, 2877