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Syndiospecific Styrene Polymerization in Aliphatic Solvents Catalyzed by FluTi(O^{i}Pr)$_3$/MAO: Study of Polymerization Conditions

Luis E. Lugo,[1,2] *Rogelio Charles,*[1] *Odilia Pérez,*[2] *Gregorio Cadenas,*[2]
*Javier Revilla**[1]

Summary: Syndiotactic polymerization of styrene in aliphatic solvents (hexane and cyclohexane) and aliphatic solvent/toluene mixtures was evaluated using a previously reported catalytic system formed by FluTi(O^{i}Pr)$_3$/MAO in order to evaluate polymerization reaction conditions and their effect on polymer tacticity. Highly syndiotactic polystyrene was produced indistinctly using pure aliphatic solvent or mixtures with toluene. On the other hand, the effect of polymerization conditions such as temperature, catalyst precursor and styrene concentrations, Al/Ti ratio and aliphatic solvent/toluene ratio over catalytic activity were analyzed.

Keywords: high-throughput screening; organometallic catalysts; polymerization; polystyrene; syndiotactic

Introduction

Since the first report of styrene syndiotactic polymerization catalyzed by a titanium precursor activated with methylaluminoxane (MAO),[1,2] several works have been done to evaluate different titanium complexes in order to improve activity, syndiospecificity efficiency and conversion, showing best results complexes with alkoxide ligands around the Ti center.[3–12] Most of these research works have been carried out using aromatic compounds as reaction solvent, such as toluene or benzene, mainly due to reasons related to precatalyst solubility and stability in these kinds of solvents. Recently, environment protection and ecological orientation are strongly considered in technology development, therefore polymerization processes based on toluene or benzene have a disadvantage compared with processes that use aliphatic solvents. Nevertheless, there are few works that have reported the use of aliphatic solvents in syndiotactic polystyrene synthesis or the analysis of reaction medium effects over the polymerization performance. Chien et al. have studied the solvent polarity effect on the catalytic activity behavior using a system formed by CpTi(OBu)$_3$ and MAO. They made experiments using pure toluene and toluene-chlorobenecene mixtures as reaction solvent, finding that the dielectric constant of the reaction medium has not effect over catalytic activity or polymer syndiotacticity.[13] Zhu et al. carried out styrene polymerization reactions using the catalytic system Cp*Ti(OC$_6$H$_4$OCH$_3$)$_3$/MAO in several reaction media, such as heptane, chlorobenzene and pure styrene. Their results suggest that the best activity values are obtained with bulk polymerization but this process presents the disadvantage of possible gelation. On the other hand, solution polymerization in heptane is better compared with experiments made in chlorobencene. They assume that this behavior is caused because solvents with higher dipolar moment have a stronger

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[1] Centro de Investigación y Desarrollo Tecnológico (CID), Lerma, México 52000
E-mail: javier.revilla@desc.com.mx
[2] Centro de Investigación en Química Aplicada (CIQA), Saltillo, México 25100

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coordination with the active species that produce syndiospecific polymerization, attributed to Ti^{III} species, decreasing the catalytic activity.[14] Entezami et al. have tested a heterogeneous titanocene catalyst for styrene syndiotactic polymerization using hexane as reaction solvent. They have studied this system with the main objective of developing a suitable heterogeneous catalyst for industrial applications, focusing on the catalyst supporting process, but they have not explored homogeneous polymerization in aliphatic or aromatic solvents in order to compare process performance.[15]

As it was mentioned before, pre-catalyst solubility and stability are important factors to select the reaction solvent, since most of the titanium complexes are only soluble in aromatic compounds. The catalytic system constituted by $FluTi(O^iPr)_3$/MAO (Flu = $C_{13}H_{19}$), previously reported by our research group,[16] has the advantage of being strongly soluble and stable in aliphatic solvents and therefore could be suitable for work in styrene syndiotactic polymerization in aliphatic solvents.

The present work discusses the feasibility of syndiotactic styrene polymerization using aliphatic solvents and aliphatic solvents/toluene mixtures. Reaction conditions fast-screening was conducted taking advantage of a high-throughput experimentation approach, using a parallel reactor system (PPR™ by Symyx). Catalytic activity dependence of temperature, catalyst precursor and styrene concentrations, MAO/Ti ratio and aliphatic solvent/toluene ratio was analyzed.

Experimental Part

Materials: Cyclohexane (Aldrich, >99% anhydrous), hexane (Aldrich, >99%) and toluene (Aldrich, >99%) were purified by reflux in solid $LiAlH_4$ for 8 hours, then were distillated on a mixture of metallic Na and benzophenone and refluxed for 6 hours to be finally distillated and recovered. Styrene (Aldrich, >98%) was purified for 6 hours using solid MAO at room temperature and finally was recovered by vacuum pressure distillation at low temperature. MAO (Aldrich, 10 wt% in toluene) was dried by toluene vacuum pressure distillation and solid MAO was used to make toluene and styrene solutions according to experimental requirements. Titanium complex Flu-$Ti(O^iPr)_3$ was synthesized according to the methodology developed by Knjazhanski et al.[16]

Polymerization: Polymerization reactions were carried out using a parallel polymerization reactor system (PPR) formed by 48 individual vessels that can hold 6 mL glass reactors inside of a controlled nitrogen atmosphere dry-box. Pressure, temperature, stirring speed and reagent addition can be controlled on-line. Solvent, styrene and MAO solution were sequentially added to each reactor; after that, reactors were heated up to set temperature, nitrogen pressure was added and stirring was started. Polymerization was initialized by injecting the pre-catalyst solution to each reactor and temperature and stirring were kept until the required reaction time was reached. Polymerization was finished adding a mixture of CO_2 and N_2; after that, reactors were taken out from the PPR and a mixture of methanol and hydrochloric acid was added to each reactor. Coagulated polymers were dried at 40 °C overnight under vacuum pressure.

Characterization: Molecular weight distribution (MWD) was obtained by gel permeation chromatography (GPC) using a Rapid-GPC by Symyx. This equipment is provided with one styragel column coupled to an evaporative light scattering detector (ELSD-Polymer Labs Inc.). O-dichlorobenzene was used as mobile phase at a flow rate of 1 mL/min at 140 °C.

Thermal analysis was carried out by differential scanning calorimetry (DSC) using a TA Instrument Q-1000. The polymer samples (4 – 5 mg) were analyzed three temperature – time programs (heating-cooling-heating) all of them at a rate of 10 °C/min. Reported melting temperature

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(T_m) and glass transition temperature (T_g) were obtained from the second heating cycle. The crystallization temperature (T_c) was obtained from the cooling cycle.

Syndiotacticity was determined by ^{13}C NMR spectroscopy in a JEOL Eclipse-300 spectrometer operating at 120 °C and 75 MHz.

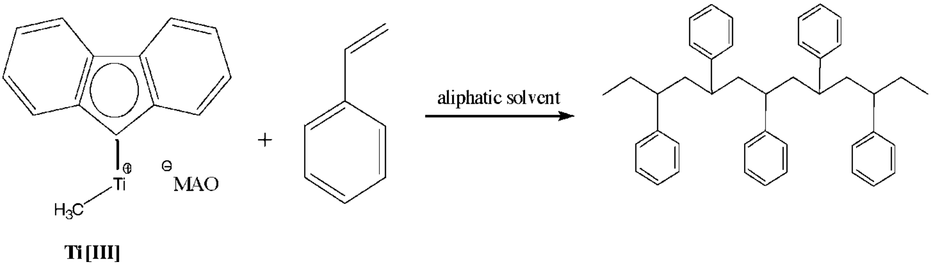
Results and Discussion

Although the nature of the activation mechanism for syndiotactic polymerization of styrene is still in discussion, most of the research literature accepts that Ti(III) cationic species has a relevant role in this process.[17–21] According to this mechanism, titanium present in the precursor complexes is reduced from Ti(IV) to Ti(III) by effect of MAO, forming a catalytic species as shown in Scheme 1. This species has the ability to promote styrene syndiotactic polymerization; hence we start from the premise that this catalytic species can be stabilized in aliphatic solvents and therefore syndiotactic polymerization is possible.

Titanium precursor concentration in the reaction medium (toluene was used as reference) was varied in order to set a suitable value for experiments with aliphatic solvents as shown in Figure 1. Considering the low conversion obtained with the three temperatures (less than 20%), it was decided to use a titanium complexes concentration of 6×10^{-4} mol/L approximately for the next polymerization.

In the same way, Figure 2 shows the effect of Al/Ti ratio variation on styrene conversion for polymerization reaction in toluene, run in order to set an optimal value for the generation of a suitable amount of polymer in the next polymerization reaction. Increasing the Al/Ti ratio improves styrene conversion, suggesting that higher Al/Ti ratios could work better for aliphatic solvents reactions. Nevertheless, sPS melting behavior of the samples obtained shows that a Al/Ti ratio increment reduces the melting peak intensity, as shown in Figure 3, reaching completely amorphous behavior at Al/Ti = 800 (corresponding to MAO concentration of 0.46 mol/L). This behavior could be caused by the presence of a high concentration of MAO oligomers, affecting crystalline domain formation of the polymer. Syndiotactic styrene polymerization in the presence of polyhedral oligomeric silsesquioxane (POSS) was reported by Coughlin et al. They found that a increase in POSS concentration causes a disruption in the crystalline behavior of sPS, since the melting peak disappears when the POSS concentration is increased.[22] It was decided to use a Al/Ti = 200 (0.115 mol/L) because in this work is more important to get crystalline behavior in sPS samples obtained in aliphatic solvents than reaching a high styrene conversion.

In order to analyze the effect of the medium polarity, polymerization reactions were carried out in pure aliphatic solvents and mixtures of aliphatic solvents with toluene. A solvent function was defined considering the toluene and total volumes,



Scheme 1.

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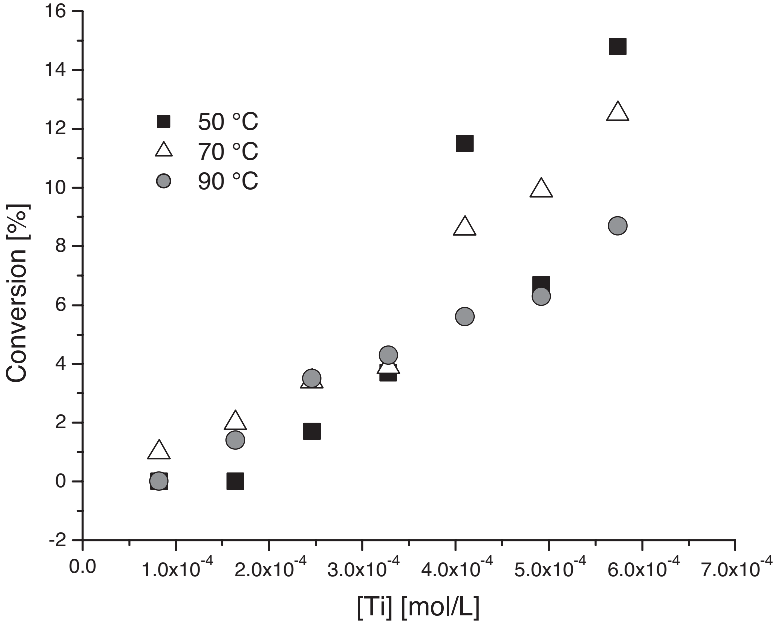

Figure 1.
Effect of titanium precursor concentration on St conversion. Solvent: Toluene; MAO/Ti = 500; [St] = 2.62 mol/L; Time = 30 min; Total vol. = 5 mL; Stir Rate = 800 rpm.

as shown in Equation 1, in order to facilitate the reagent addition in the experimental design. A value of $S(V_{toluene}) = 0$ means pure toluene in the reaction whereas $S(V_{toluene}) = 1$ means pure aliphatic solvent.

$$S(V_{toluene}) = \frac{(V_{total} - V_{toluene})}{V_{total}} \tag{1}$$

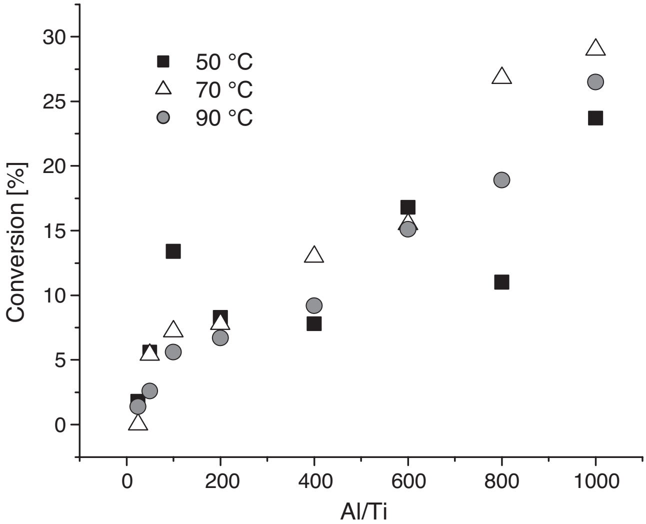

Figure 2.
Al/Ti ratio effect on St conversion. Solvent: Toluene; [Ti] = 5.74×10^{-4} mol/L; [St] = 2.62 mol/L; Time = 30 min; Total vol. = 5 mL; Stir Rate = 800 rpm.

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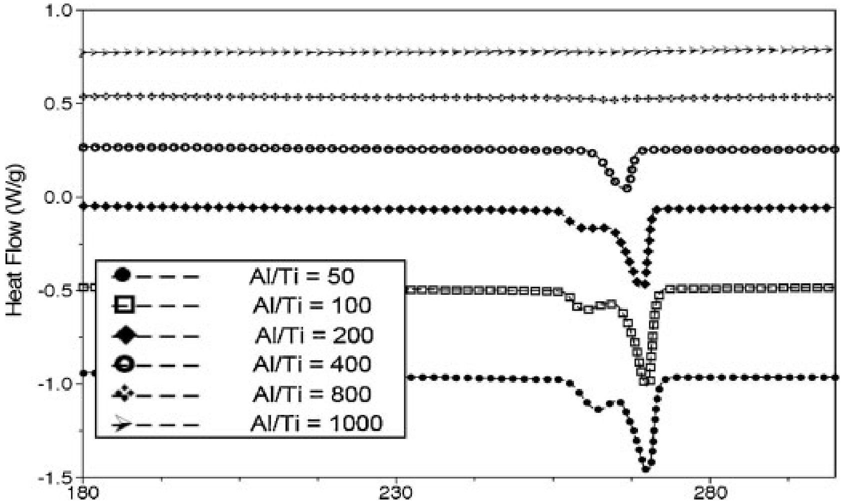

Figure 3.
Al/Ti ratio effect on melting temperature peak (Reaction temperature = 70 °C).

By way of example, results for some representative cases of polymerizations carried out using cyclohexane, hexane or a mixture with toluene at 3 different temperatures are shown in Table 1. It is remarkable that conversion, and therefore catalytic activity, is higher in reactions made in pure aliphatic solvent than in those made with toluene.

The syndiotactic index (SI) is normally calculated as the polymer insoluble fraction in boiling 2-butanone since this methodology is easy and it does not require ^{13}C-NMR analysis. Nevertheless, we have observed that samples obtained from PPR reactors showed low SI values, contrary to results from samples obtained in a previous work in a 100 mL reactor.[16] Using thermo gravimetric analysis (TGA), we have compared samples after and before boiling 2-butanone extraction, and we have observed a weight loss before 100 °C, as

Table 1.
Representatives examples of polymerization results carried out in aliphatic and aliphatic/toluene mixtures[a)].

Aliphatic Solvent	Reaction Temperature [°C]	$S(V_{toluene})$	Yield [g]	Convn. [%]	Activity[b)]	SI[c)] [%]	T_m [d)] [°C]	ΔH_m [d)] [J/g]	T_g [d)] [°C]	Mw [e)] $\times 10^{-3}$	PDI [e)]
Cyclohexane	50	0.125	0.106	7.8	73.8	97.2	270.4	53.2	100.6	277.1	8.6
Cyclohexane	50	1	0.697	51.1	485.4	99.1	269.0	52.5	100.9	667.1	2.8
Cyclohexane	70	0.125	0.252	18.4	175.2	97.3	270.1	53.4	100.5	196.7	4.8
Cyclohexane	70	1	0.445	32.6	310.0	98.8	269.1	56.6	100.3	346.1	3.4
Cyclohexane	90	0.125	0.158	11.6	110.2	97.6	269.3	46.3	99.1	90.5	3.9
Cyclohexane	90	1	0.232	17	161.4	99.5	270.1	63.9	100.8	151.1	3.8
Hexane	50	0.125	0.197	14.5	137.4	98.4	270.2	63.1	99.7	242.5	7.4
Hexane	50	1	0.661	48.4	460.3	95.9	268.0	50.0	100.8	577.3	2.5
Hexane	70	0.125	0.250	18.3	174.1	93.1	269.4	40.1	96.4	161.3	4.5
Hexane	70	1	0.367	26.9	255.6	99.4	269.2	58.6	100.8	362.2	3.0
Hexane	90	0.125	0.201	14.7	140.1	92.6	270.2	57.6	99.6	85.9	4.2
Hexane	90	1	0.342	25.1	238.2	94.3	270.0	50.9	100.9	172.4	3.7

[a)] [Ti] = 5.74×10^{-4} mol/L; Al/Ti = 200; [St] = 2.62 mol/L; Time = 30 min; Stir speed = 800 rpm;

[b)] in kgPS/mol Ti*hr.

[c)] polymer insoluble fraction in boiling 2-butanone after thermal treating whose tacticity was obtained by ^{13}C-NMR;

[d)] obtained from second heating cycle at 10 °C/min;

[e)] obtained at 140 °C in o-dichlorobenzene.

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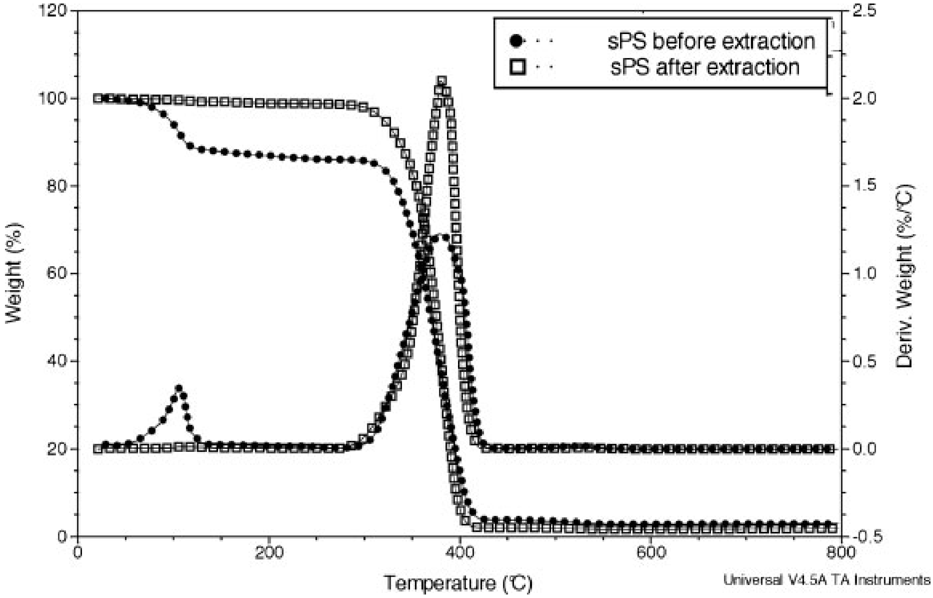

Figure 4.
Weight loss for a sPS sample before and after boiling 2-butanone extraction.

exemplified in Figure 4. This behavior suggests that absorbed solvent is present inside the polymer, despite the drying process of the sample, and a thermal treatment (heating to 180 °C) was necessary in order to remove the remaining solvent before 2-butanone extraction. Using this process it was possible to obtain SI values higher than 90%, as shown in Table 1.

Syndiotacticity for samples obtained with $FluTi(O^{i}Pr)_3/MAO$ catalytic system in aliphatic solvents was confirmed by ^{13}C-NMR at 100 °C, as shown in Figure 5. Carbon assignments for the corresponding chemical shift are marked in the spectra. Typically, a chemical shift at 145.5 ppm has been related to phenyl C_1 carbon with syndiotactic configuration, unlike isotactic (C_1 at 146.24 ppm) and atactic configurations (five peaks in the range of 145.1–146.7 ppm).[1,23] Polymer samples obtained in aliphatic solvent show this single peak at 145.5 ppm, confirming their syndiotactic nature.

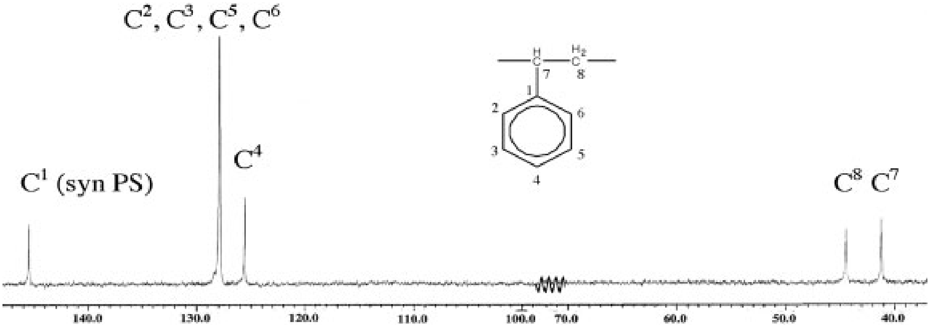

Figure 5.
^{13}C-NMR for sPS obtained in pure cyclohexane.

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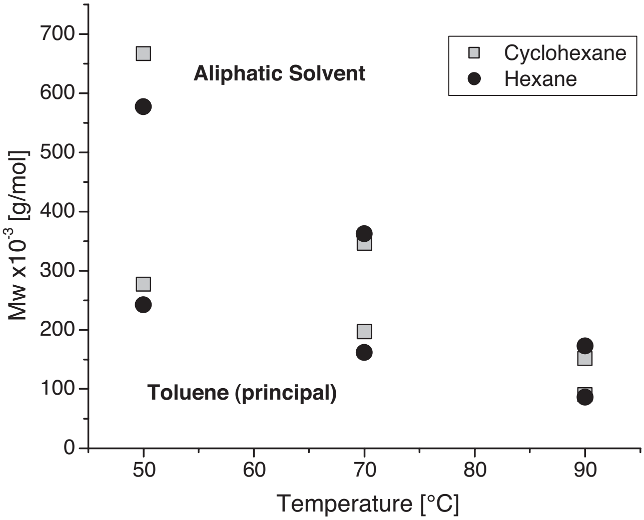

Figure 6.
Temperature and solvent effect over molecular weight (Mw) of sPS.

On the other hand, the molecular weight of sPS was affected by reaction temperature and kind of solvent, as shown in Figure 6. Polymers obtained in aliphatic solvents show higher molecular weight than polymers synthesized in toluene as principal component. These results suggest that the ratio of (propagation rate)/(chain transfer rate) is higher in polymerizations carried out in aliphatic media than in those made in aromatic media. Considering that higher conversion values were obtained in alipha-

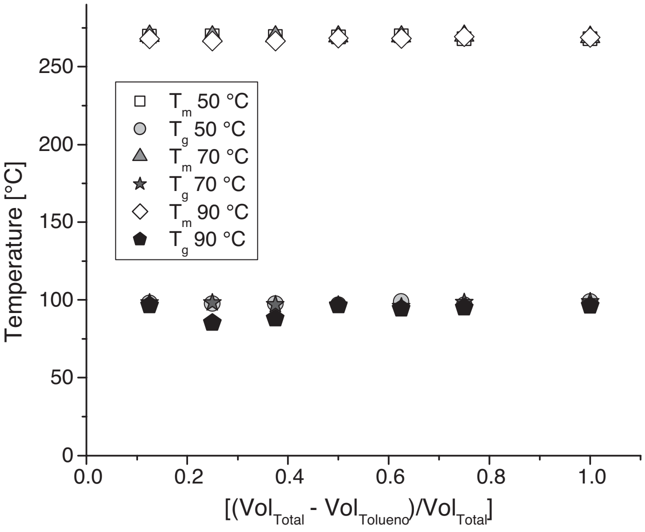

Figure 7.
Melting and glass transition temperatures for sPS obtained in pure cyclohexane and cyclohexane/toluene mixtures.

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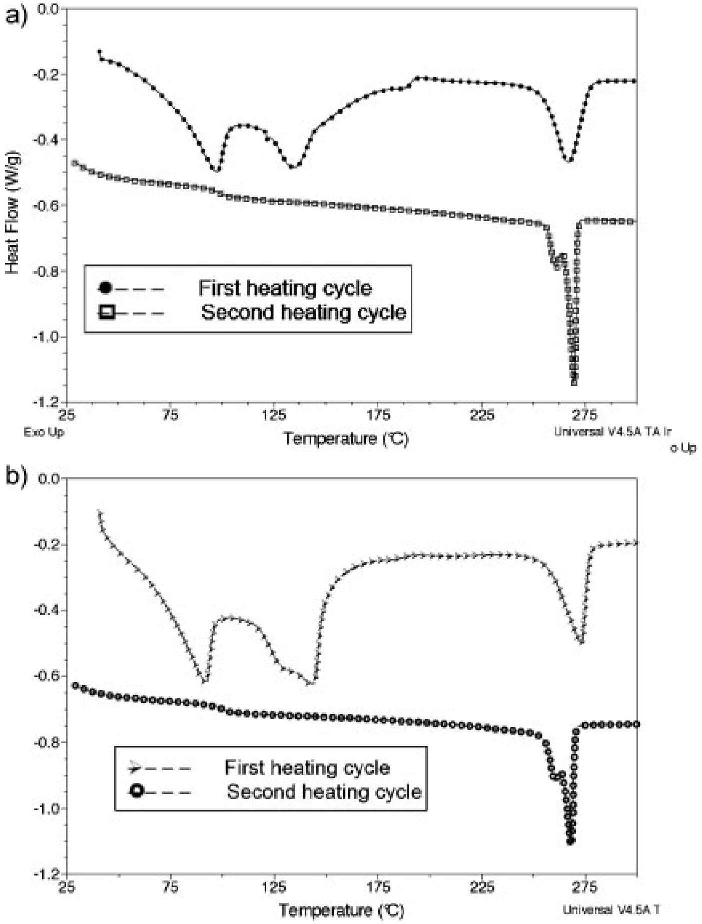

Figure 8.
Polymorphism showed by a sPS sample obtained in a) hexane and b) toluene.

tic solvents, the propagation rate in hexane and cyclohexane could be higher than that in toluene, whereas the chain transfer rate does not increase as much as the propagation rate. In all cases, Mw decreases as the reaction temperature is increased and no significant difference was observed using hexane or cyclohexane.

Melting behavior does not show any dependence of reaction medium polarity, as observed in the values of melting temperatures in Figure 7. Likewise, glass transition temperature does not show significant variations with the use of pure aliphatic or aliphatic/toluene mixtures. These results suggest that the polarity of the solvent medium has not an important effect on syndiotactic polystyrene polymerization.

Polymorphism in sPS obtained under several conditions and using different catalytic systems has been observed by DSC analysis and reported in several works.[4,13,14,23] During the first heating cycle in DSC analysis, sPS samples synthesized in both aliphatic solvents and toluene show endothermic transitions in the temperature range of 75–150 °C, whereas at 270 °C display a single melting peak, as shown in Figure 8. Nevertheless, after the cooling cycle and during the second heating cycle, transitions between 75–150 °C disappear and two peaks are displayed in the range of 260 to 275 °C, indicating the presence of polymorphism in the crystalline domains of sPS.

The styrene concentration effect over activity at different temperatures is shown in Figure 9. In general, as styrene content was increased catalytic activity improved. It is remarkable that the polymerization reaction can be made at room temperature (20 °C) with the FluTi(O^{i}Pr)$_3$/MAO catalytic system, since this allows for possible block copolymerization with butadiene.[24–26] On the other hand, decreasing activity was observed at 70 °C and high styrene concentration. This behavior could be related to a gelation effect produced by strong molecular interactions between crystalline sPS and styrene, as it was reported in previous works using similar conditions of reaction temperature and styrene concentration.[27,28] The syndiotactic polystyrene gel is not a chemically crosslinked gel but a physical gel with monomer molecules intercalated between polymer chains; such gel tends to precipitate due to high insolubility in styrene and organic solvents. Gel formation can affect the polymerization rate due to mass transfer resistance exerted by the presence of a polymer solid phase, decreasing catalytic activity and molecular weight.

Finally, the molecular weight shows dependence of styrene concentration variation during polymerization in aliphatic solvent, as shown in Figure 10. Below [St] = 6 mol/L, the Mw increases with [St] increments, but above this concentration, Mw shows a decreasing tendency. This behavior can be due to sPS gel formation, as it was explained before, since polymerization rate is decreased by the presence of the polymer solid phase.

Conclusions

Syndiospecific styrene polymerization can be carried out in toluene/aliphatic solvent mixtures and pure aliphatic solvent obtaining highly syndiotactic polymers. The effect of several experimental variables on polymerization reaction was analyzed, finding that increments of Al/Ti ratio, catalyst and styrene concentrations produce higher conversion and activity.

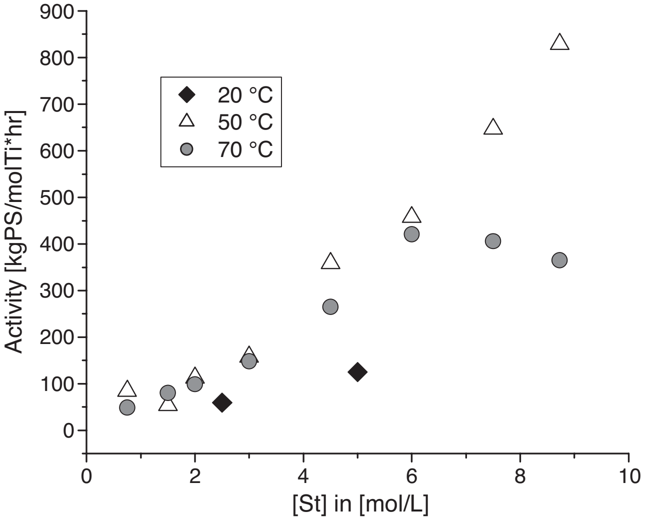

Figure 9.

Styrene concentration effect on catalytic activity. Solvent: Cyclohexane; Al/Ti = 200; [Ti] = 5.74×10^{-4} mol/L; Time = 30 min; Total Vol. = 5 mL.

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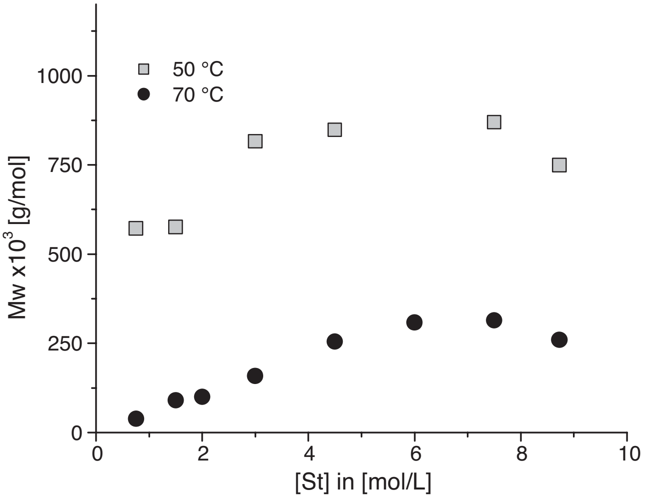

Figure 10.
Styrene concentration effect on molecular weight. Solvent: Cyclohexane; Al/Ti = 200; [Ti] = 5.74×10^{-4} mol/L; Time = 30 min; Total Vol. = 5 mL.

On the other hand, crystalline polymorphism was found in samples obtained with aliphatic solvents, whereas the melting peak disappears whit high MAO concentrations.

High-throughput experimentation proves high efficiency to carry out reaction conditions evaluation in syndiospecific styrene polymerization.

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