J. Chil. Chem. Soc., 58, Nº 4 (2013)

FURTHER STUDIES ON HOMO- AND COPOLYMERIZATION OF STYRENE THROUGH $CpTiCl_3$-MAO INITIATOR SYSTEM.

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(Received: July 30, 2013 - Accepted: October 30, 2013)

ABSTRACT

The copolymerization of styrene with cyclohexene, 1-methyl-1-cyclohexene and with norbornene at various styrene/comonomer molar ratio, using cyclopentadienyltitanium trichloride and methylaluminoxane, $CpTiCl_3$-MAO, initiating system has been tested. Only the couple styrene-norbornene produce real styrene-norbornene copolymers, while comonomers cylohexene and 1-methyl-1-cyclohexene only yielded syndiotactic polystyrene, s-PS. The present paper also report results of exploratory experiments on the synthesis through in-situ polymerization of nanocomposites based on styrene/para-methylstyrene copolymer, S/p-MeS, including SiO_2 nanoparticles where nanocomposites with modified SiO_2 nanoparticles, showed a better dispersion of nanoparticles in the copolymer matrix.

Keywords : styrene, substituted styrene, cycloalkenes, nanocomposites, metallocene catalysts, polymerization

INTRODUCTION

In the early 1950s G. Natta et al., discovered isotactic polystyrene, i-PS,[1,2] a semicrystalline stereoregular polymer with a T_m of 240 ºC but with a low rate of crystallization. Latter Zambelli et al.[3] and Ishihara et al.[4] informed about the obtainment of syndiotactic polystyrene, s-PS, with a T_m of 270 ºC and a fast rate of crystallization. Anyhow these new type of polystyrenes show some deficiencies: are brittle with low impact resistance, and need a rather high processing temperature. Since that time, several research groups, both from academy and from industry, have been engaged in homo- and copolymerization of styrene. A large number of initiating systems, from Ziegler-Natta catalysts till metallocene catalysts have been studied. As result of those research works interesting and efficient systems have been reported.

Regarding cycloalkene comonomers, it is known that due to their structure cycloalkenes can experiment two possible polymerization routes : through the carbon-carbon double bond or by a ring-opening (olefin metathesis) reaction, as for example, for cyclobutene. Each of the two polymerization routes can yield two stereoisomers poly(1,2-cyclobutylene), resulting from C-C double bond polymerization, can exist as either the erythrodiisotactic or erythrodisyndiotactic isomer. While ring-opening polymerization generate poly(1-butenylene) which is the same polymer as obtained by the 1,4-polymerization of 1,3-butadiene and can exist as either the cis or trans isomer. Each of the four isomeric polymers has been observed in the polymerization of cyclobutene. Exclusive polymerization through the double bond does not occur with any other cycloalkenes. Cyclohexene does not polymerize by either route in the presence of various initiators except when the cyclohexene structure is part of a bicyclic system as in norbornene. Cycloheptene and higher cycloalkenes undergo only ring-opening polymerization.[5]

Zambelli et al., reported that half-titanocenes $(\eta\text{-}C_5H_5)TiCl_3$ and $(\eta\text{-}C_5H_5)_2TiCl_2$ after reaction with methylaluminoxane, MAO, yield very efficient and versatile homogeneous catalysts that promote polymerization of styrene and alkyl substituted styrene to highly syndiotactic polymers.[6]

We studied the copolymerization of styrene with p-methylstyrene [7,8] concluding that styrene reactivity is increased by I+ inductive effect of substituents placed in the para position, by polar solvents, and that steric hindrance near the vinyl group of styrene decreases the reactivity related to styrene. On the other hand our results indicate that thermal behaviour of S/p-MeS copolymer is improved and Tg values increase with content of p-MeS in the copolymer.[8]

In our research group we have been studying the homo- and copolymerization of styrene through metallocenic polymerization using diphenylzinc-metallocene-MAO initiating systems. The initial objective was to produce styrene with improved properties compared to conventional polystyrene. Titanium, zirconium and hafnium metallocene were used, establishing that catalyst efficiency follows the order titanocene > zirconocene > hafnocene.[9] Besides the use of these metallocenes, a kind of comonomers were studied : substituted styrene (alkylstyrenes,[10] methoxistyrene[11]) styrene derivatives (α-methylstyrene[12]). By the other hand styrene/alkene[13] and styrene/diene[14] copolymerizations were also studied . Our results indicate that titanocenes produced almost pure syndiotactic styrene, s-PS, while circonocenes produced mostly atactic polystyrene, a-PS, with 10-15 % of s-PS content. In our early research we had concluded that titanocene-MAO systems are more active catalysts than zirconocene-MAO, and they favour stereoregular (syndiotactic) styrene polymerization, and for substituted styrenes, depending on the substituent's position, are more reactive those with withdrawing-electron capacity favour yield and stereoregularity producing almost pure syndiotactic polymer.[9,10] In 1995 Zambelli et al. indicate that polymerization of substituted styrene is increasingly stereospecific in the order : p-chlorostyrene < styrene < p-methylstyrene.[15] Regarding homopolymerization of alkenes, zirconocenes were the most effectives, particularly regarding those with long carbon chains such as hexa- and octadecene.[13]

More recently our group started a new research line including nanoparticles and nanocomposites linked to styrene and olefin polymerization. We are doing exploratory research through in-situ polymerization of styrene/p-methylstyrene including SiO_2 nanoparticles.

In the present paper we report on the our most recent work on metallocene-MAO homo- and copolymerization of styrene with cycloalkenes through $CpTiCl_3$-MAO and highlight the formation of nanocomposites based poly(styrene-co-para-methylstyrene) including SiO_2 nanoparticles, by in-situ copolymerization.

EXPERIMENTAL

Homo- and copolymerization experiments were carried out in an argon atmosphere in a 100 cm^3 Schlenk tube equipped with a magnetic stirrer. Solvent toluene (ca. 10 to 30 cm^3), MAO solution, and metallocene solutions in toluene were charged sequentially by syringe under argon pressure. Polymerization was initiated by injecting either the styrene followed by the comonomer, or both of them simultaneously. The reactions were kept at 60 °C under stirring for the required length of time. Polymerization was terminated by adding a mixture of hydrochloric acid and methanol. The polymers, coagulated in the acidified methanol, were recovered by filtration after washing several times with methanol, and dried under vacuum at 60 °C.

SiO_2 were prepared accordingly the sol-gel method as described in previous papers.[16]

Viscosities were measured either in chloroform or in o-dichlorobenzene, depending on the solubility of the polymer, and intrinsic viscosities were determined by the one-point method.[17]

DSC analyses were made by using a Rheometrics Scientific DSC apparatus with samples placed in a nitrogen atmosphere. 3 to 4 mg samples were heated at a rate of 10 °C/min, and after cooling to room temperature, reheated at the same rate. The reported Tg and Tm were those obtained in the second heating scan.

^{1}H-NMR spectra were recorded on a Bruker AMX-300 spectrometer at

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60 °C, operating at 300.1 MHz. The polymers and copolymers were dissolved in deuterated 1,1,2,2-tetrachloroethane ($C_2D_2Cl_4$, 5% w/v). A total of 64 scans with 16K data points and with a relaxation delay of 1 second were collected. Chemical shifts were calibrated with tetramethylsilane (TMS) used as internal reference.

RESULTS AND DISCUSSION

In a previous paper we have report on the homo- and copolymerization of styrene with cyclohexene, CyHex, with (1-methyl-1-cyclohexene), MeCyHex, and with bicyclo[2.2.1]hept-2-ene or norbornene, Norb, using bisindenylzirconnium dichlorid -MAO, $Et(Ind)_2ZrCl_2$-MAO, as initiator system.[18] In the present paper we tested a half-sandwich titanocene-MAO initiator system: cyclopentadienyltitanium trichloride-methylaluminoxane, $CpTiCl_3$-MAO.

Table 1 shows the results of the copolymerization of styrene-cyclohexene and of styrene 1-merthyl-1-cyclohexene by the $CpTiCl_3$-MAO initiator system. The results indicate of a very low or nil incorporation of the cycloalkene to the polymer chain. On the other hand, it was also noted that the polymer obtained isi almost pure syndiotactic polystyrene in agreement with the low or nil polymerization capacity of cycloalkenes. However, these figures indicate that cycloalkenes, and particularly the methyl substitution on the vinyl carbon of cyclohexene decrease the molecular size of resulting polymer as the proportion of such comonomers in the polymerization initial feed increased, which can be attributed to a sort of coordination active species-carbon double bond of the comonomer which inhibit the polymer propagation.

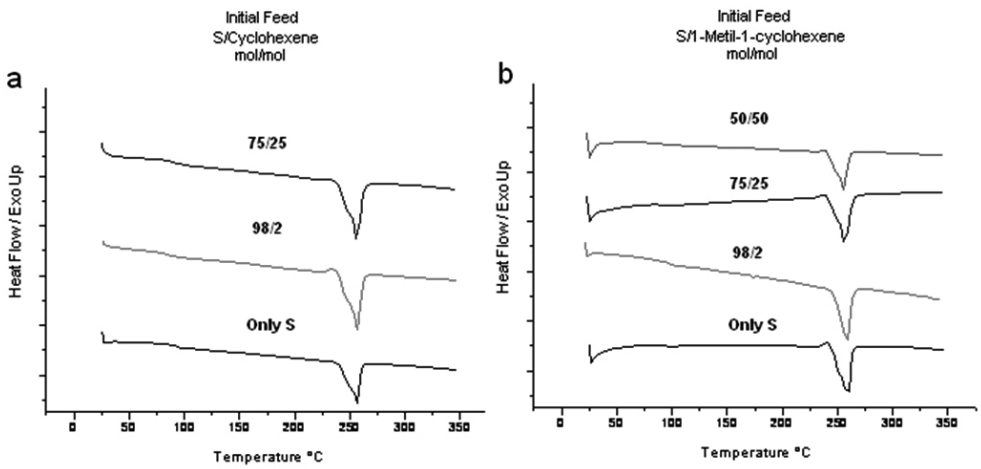

Fig. 1 DSC thermograms of polymer resulting from a) : Styrene/cyclohexene and b) : Styrene /(1-methyl-1-cyclohexene) copolymerization using the $CpTiCl_3$-MAO initiator system in toluene at 60 °C during 48 hours

In Figure 1 it is seen that the thermograms are in agreement with s-PS but not with a copolymer S/CyAlk, indicating that neither cyclohexene nor 1-methyl-1-cyclohexene are incorporated in the polymer chains. This agrees with the ^{1}H-NMR analysis (Fig. 2). It also agrees with what was already mentioned, that cyclohexene does not polymerize by either route, i.e., through C-C double bond or by ring-opening polymerization, in the presence of various initiators.[5]

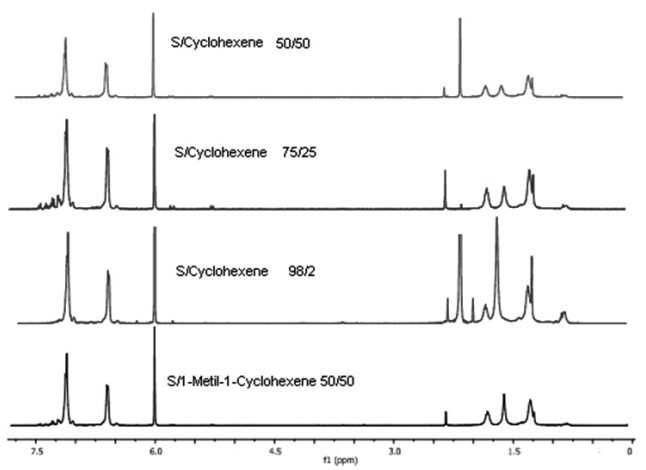

Figure 2, ^{1}H-NMR spectra in $CDCl_3$ at 60 °C of products obtained from S/Cycloalkene Copolymerization using $CpTiCl_3$ initiator system in toluene after 48 hours at 60 °C. S/CyAlk (mol/mol) ratios in the initial feed are indicated for each spectrum

Table 2, shows the results of styrene/norbornene polymerization where it is seen that conversion to copolymer decrease as the norbornene proportion in the feed increases confirming the lower capacity of norbornene to become incorporated in the growing copolymer chain. Anyhow, the norborned was more reactive than the previous two cycloalkenes, in agreement with stated polymerization reactivity capacity. The resulting copolymers present lower molecular weights than those obtained for polystyrene polymerized by this CpTiCl3-MAO initiator catalyst system.

Furthermore, the resulting copolymers showed lower norbornene content than that in the initial feed, pointing to its lower reactivity compared to styrene. According to the molecular weight distribution, the values for the copolymer obtained are in agreement with a metallocenic polymerization process which is narrow and between 1.03 and 1.40. These results indicate that norbornene it is more reliable to copolymerize with styrene when compared with the monocyclic alkenes studied.

The copolymer composition S/Norb were calculated from their ^{1}H-NMR spectra which indicated that norbornene incorporation was lower than its proportion in the initial feed. Runs S/Norb = 75/25 and 50/50 mol/mol in initial feed yielded respectively only 12.2 and 32.4 % mol norbornene contents. In agreement with its lower reactivity compared with styrene.

Table 1. Copolymerization styrene/cycloalkene using $CpTiCl_3$-**MAOas intiating system, in toluene after 48 hours at 60 °C.**[a]

Initial feed S/CyAlk mol/mol	CyAlk in initial feed mmol	Yield wt%	|η|b dL/g	Activity ratioc	DSC Tg °C	DSC Tm °C
Styrene / Cyclohexene						
Only S	0.00	60.5	0.43	1.00	98	257
95/2	1.58	59.7	0.28	1.03	97	257
75/25	1.98	54.4	0.47	0.91	91	n.s.
CyHex	------	------	------	------	------	------
Styrene / 1-Methyl-1-cyclohexene						
Only S	0.00	82.7	0.19	1,00	93	259
95/2	0,91	63.0	0.17	1.11	101	261
75/25	10.8	54.0	0.14	0.11	92	260
MeCyHex	------	------	------	------	------	------
Initial feed S/CyAlk mol/mol	**CyAlk in initial feed mmol**	**Yield wt%**	**|η|[b] dL/g**	**Activity ratio[c]**	**DSC Tg °C**	**DSC Tm °C**
Styrene / Cyclohexene						
Only S	0.00	60.5	0.43	1.00	98	257
95/2	1.58	59.7	0.28	1.03	97	257
75/25	1.98	54.4	0.47	0.91	91	n.s.
CyHex	------	------	------	------	------	------
Styrene / 1-Methyl-1-cyclohexene						
Only S	0.00	82.7	0.19	1,00	93	259
95/2	0,91	63.0	0.17	1.11	101	261
75/25	10.8	54.0	0.14	0.11	92	260
MeCyHex	------	------	------	------	------	------

[a]Copolymerization conditions: Total volume = 25 mL; [S] + [comonomer] = 2.0 mol/L; $[CpTiCl_3]$ = 2.0E-04 mol/L. [b]Measured in 1,2-dichlorobenzene and calculated according to the one-point approximation method [19]. [c]Activity ratio: referred to that of styrene arbitrarily defined as equal to 1. n.s. = No signal.

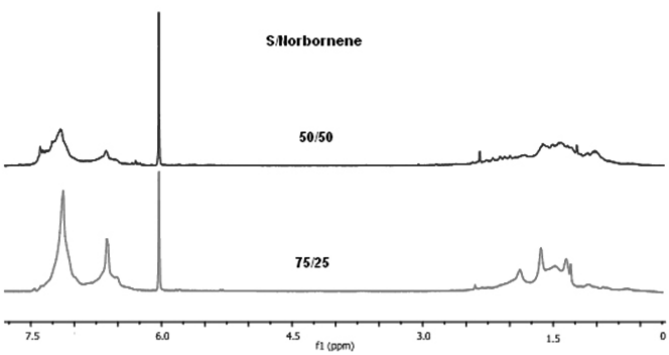

Figure 3, ^{1}H-NMR spectra in CDCl3 at 60 °C of S/Norbornene copolymers Obtained with the $CpTiCl_3$ initiator system in toluene after 48 hours at 60 °C. S/Norb (mol/mol) ratios in the initial feed are indicated for each spectrum.

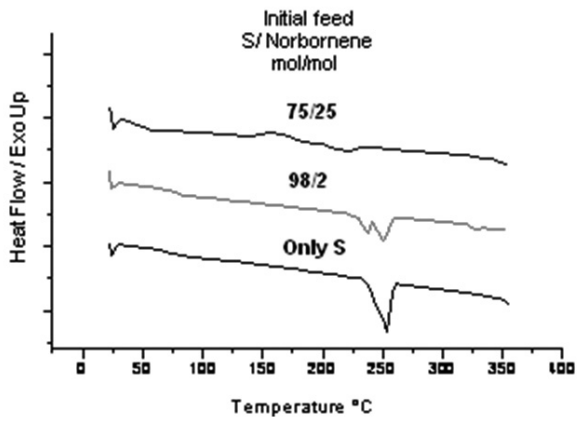

Figure 4. DSC thermogram of products from S/norbornene copolymerization with the $CpTiCl_3$ initiator system, in toluene after 48 hours at 60 °C. S/Norb (mol/mol) ratios, in the initial feed, are indicated for each spectrum.

Table 2. Copolymerization styrene/norbornene by $CpTiCl_3$-MAO initiating system, after 48 hours at 60 °C.[a]

Initial fee[d] S/ Norb mol/mol	Norbin initial feed mmol	Yield Wt%	ıηı[b] dL/g	Activity Ratio[c]	GPC Mn g/mol	GPC Mw g/mol	GPC IP	DSC Tg °C	DSC Tm °C
Only S	0	42.1	0.23	1.00	60100	77900	1.30	77	254
98/2	1.04	37.7	n.d.	0.31	Insol	------	-----	78	251
95/5	2,39	18,1	0,14	0.39	49637	61151	1.23	n.d.	-----
90/10	4,79	4,9	0,14	0.10	53444	72998	1.37	n.d.	-----
75/25	12,9	12,5	0.11	0.22	37164	37164	1.03	57	218
50/50	26,2	9.4	0,10	0.17	Insol	------	----	n,d.	-----
25/75	39,5	5.9	0,07	0.11	n.d.	-----	----	n.d.	-----
Only Norb	5.00	n.d.	n.d.	0.02	n.d.	-----	----	n.d.	n.d.

[a] Copolymerization conditions: Total volume = 25 mL; [S] + [comonomer] = 2.0 mol/L; obtained with the $CpTiCl_3$ initiator system in toluene after 48 hours at 60 °C. $[CpTiCl_3]$ = 2.0E-04 mol/L. [b] Measured in 1,2- dichlorobenzene and calculated according to the one point approximation method.[17] [c] Activity ratio: referred to that of styrene arbitrarily defined as equal to 1. n.d. = No determined.

In the last two years our Group has been working on nanocomposites through in-situ metallocenic polymerization.[19,20,21] More recently exploratory research has been under way, and exploratory studies on the synthesis of nanocomposites obtained through in-situ copolymerization including styrene, p-methylstyrene and SiO_2 nanoparticles using CpTiCl3-MAO initiator system have been performed.

Table 3 reports the results of the styrene/p-methylstyrene copolymers and of those in which 5% of SiO_2 nanoparticles, Nps, were included in the initial feed, and of a third situation where hexadecytrimethylsilane-modified nanoparticules, modified-Nps, were included at the initial feed of the polymerization reaction. The nanoparticles were modified with hexadecytrimethylsilane to improve their dispersion in the copolymer. From these results is noted that conversion to copolymer increase with the growth up of p-MeS in the initial feed, a known effect already reported [7,9]. This effect it is maintained in experiment including Nps with and without modification. Those with unmodified Nps yield almost the same as those resulting from plain nanocomposites with similar composition in the initial feed.

Table 3. Nanocomposites S/p-MeS-SiO_2 nanoparticles obtained by in situ polymerization using $CpTiCl_3$-MAO initiator system in toluene at 60 °C after 30 minutes. [a]

S/p-MeS mol/mol	Yield wt%	ıηı[b] dL/g	DSC Tg °C	DSC Tm °C	Yield wt%	ıηı[b] dL/g	DSC Tg °C	DSC Tm °C	Yield wt%	ıηı[b] dL/g	DSC Tg °C	DSC Tm °C
	Without NPs				With 5% SiO_2 NPs				With 5% SiO_2 modified-NPs			
S only	59	0.15	78	248	66	0.17	88	239	57	0.13	79	234
95/5	59	0.15	80	232	71	0.17	85	223	60	0.14	n.d.	n.d.
50/50	80	0.16	82	n.s.	81	0.12	81	n.s.	61	0.15	96	n.s.
5/95	95	0.16	94	n.s.	92	0.10	98	n.s.	63	0.16	78	n.s.
p-MeS only	97	0.16	90	n.s.	94	0.10	88	n.s.	100	0.16	97	n.s.

[a] Copolymerization conditions: Total volume = 25 mL; [S] + [comonomer] = 2.0 mol/L; $[CpTiCl_3]$ = 2.0E-04 mol/L. [b] Measured in 1,2- dichlorobenzene and calculated according to the one point approximation method.[17 [c] Activity ratio: referred to that of styrene arbitrarily defined as equal to 1. NPs = nanoparticles, n.d. = not determined, n.s.= no signal.

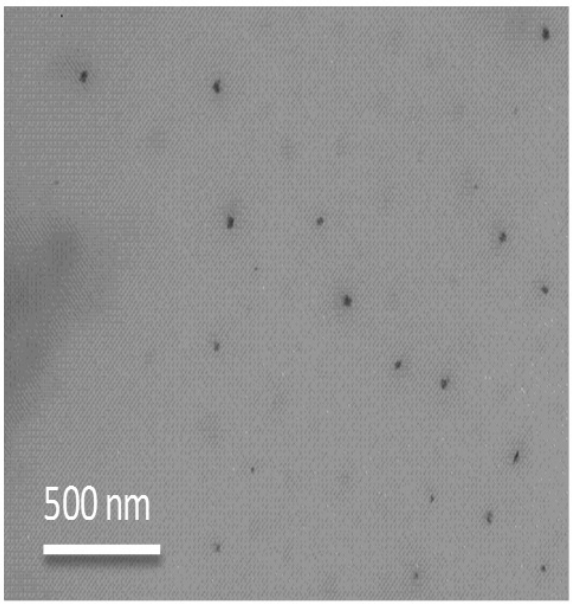

Figure 5, TEM image of composite obtained by in-situ polymerization of S/p-MeS + 5% SiO_2 Mod-Nps, through CpTiCl3 – MAO initiator system in toluene after 6 h at 60 °C.

A similar behavior it is seen for intrinsic viscosity. While the Tg value increases slightly when passing from P(S-co-pMeS) to those with 5 % (w/w) Nps, modified or unmodified. TEM analysis shows that Nps dispersion in the copolymer mass improves for the modified-Nps reaching the desirable effect. Samples have been sent to an external laboratory for mechanical resistance measurements. In Fig. 5 it is shown the TEM image of obtained nanocomposite P(S-co-pMeS) with 5% of modified SiO_2.

CONCLUSIONS

- Polymerization of styrene with cyclohexene and with para-methylcyclohexene through the $CpTiCl_3$-MAO initiator system, under the given experimental conditions produced only syndiotactic polystyrene.
- Polymerization of styrene-norbornene through the CpTiCl3-MAO initiator system, produced truly P(styrene-co-norbornene) with the incorporation of norbornene in the resulting copolymer lower than its proportion in the initial feed of the polymerization.
- Exploratory results of synthesis through in-situ polymerization of styrene – para-methylstyrene and SiO_2 NpS, using $CpTiCl_3$-MAO initiator system produce the corresponding nanocomposite.

ACKNOWLEDGEMENTS

Financial support from Departamento de Investigaciones Científicas y Tecnológicas, Universidad de Santiago de Chile, DICYT-USACH, and from FONDECYT Project Nr. 108.5061 and Nr. 11110237 are gratefully acknowledged.

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