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Comparative study of homogeneous and heterogeneous styrene polymerizations with $Ni(acac)_2$/MAO catalytic system

Luis Carlos Ferreira Jr., Marcos A.S. Costa, Pedro Ivo C. Guimarães,
Luiz Claudio de Santa Maria*

Grupo de Polímeros, Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, CEP 20559-900 Rio de Janeiro, Brazil

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Abstract

Styrene polymerization was carried out with $Ni(acac)_2$/MAO and $Ni(acac)_2/SiO_2$/MAO. The influence of reaction parameters (Al/Ni mole ratio, catalyst concentration, temperature and time polymerization) on styrene polymerization was evaluated. It was observed that both catalytic systems were affected by reaction parameters and that the heterogeneous catalyst presented higher activity than the homogeneous one. Polystyrenes with different molecular weight, stereoregularity and polydispersity were obtained. These results suggest that different active catalyst species could have been present. In addition, two types of methylaluminoxane (MAO) with different molecular weights were also evaluated as cocatalyst. As a result, the catalyst activity and stereospecificity were strongly affected by the MAO type. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nickel acetylacetonate; Polystyrene; Coordination polymerization

1. Introduction

Since the discovery of Ziegler–Natta catalysts [1–4], much effort has been made to focus the improvement of stereospecific polymerization. However, insufficient data reports have been published on the use of transition metal acetylacetonates with MAO as cocatalyst for ethylene [5], dienes [6–9], acrylic monomers [10–14] and styrene [15–17] polymerizations.

It is known that styrene polymerization with soluble catalyst based on nickel acetylacetonate/methylaluminoxane [$Ni(acac)_2$/MAO] produces isotactic polymers with low molecular weight [15–17]. In the last years, different inorganic supports and distinct catalyst impregnation procedures used for styrene polymerization were described in the literature [18–25]. Nevertheless, the investigation of methods for impregnation of $Ni(acac)_2$ on SiO_2/MAO [25] and the effect of reaction parameters on styrene polymerization still remain incomplete. As is well-known, MAO is a common cocatalyst cited in literature for styrene polymerization with $Ni(acac)_2$. Furthermore, to the best of our knowledge, the effects of MAO molecular weight (dependent of trimethylaluminium content) [26] on the heterogeneized catalyst supported on SiO_2 have not been studied.

The aim of this work is to report some results about the effect of MAO molecular weight on styrene polymerization with the use of catalytic systems based on $Ni(acac)_2$/MAO and $Ni(acac)_2/SiO_2$/MAO. Moreover, it has also investigated the influence of some polymerization parameters on styrene polymerization.

2. Experimental

2.1. Material

Toluene was refluxed over sodium/benzophenone. The styrene was purified by distillation over CaH_2 before use. $Ni(acac)_2$ was dried by toluene azeotropic distillation. MAO [Witco ($M_w = 800–1200$)] and MAO [Akzo ($M_w = 1500–2000$)] 10 wt% in toluene suspension (kindly supplied by Witco and Akzo) were used as received. SiO_2 Aldrich (MS3070) with 700 m^2/g was employed as catalyst support. Nitrogen was purified by passing it through molecular sieves (3 Å) and P_2O_5 columns.

2.2. Supported catalyst preparation

SiO_2 was calcinated at 400 °C for 4 h under nitrogen

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* Corresponding author. Tel.: +55-21-2598-7322; fax: +55-21-2587-7227.

E-mail address: lcsm@uerj.br (L.C. de Santa Maria).

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$$[\text{-Al(Me)O-}]_n \cdot x\text{AlMe}_3 \rightleftharpoons [\text{-Al(Me)O-}]_n.(x - y)\text{AlMe}_3 + y\text{AlMe}_3 \quad \text{(a)}$$

$$\text{Me}_2\text{Al-O-[Al(Me)-O]}_n\text{-AlMe}_2 + \text{AlMe}_3 \rightleftharpoons$$

$$\text{Me}_2\text{Al-O-[Al(Me)-O]}_{n-x} - \text{AlMe}_2 + \text{Me}_2\text{Al} - \text{O} - [\text{Al(Me)} - \text{O}]_{x-1} - \text{AlMe}_2 \quad \text{(b)}$$

$$\text{AlMe}_3 + \text{MAO} \rightleftharpoons \text{MAO[AlMe}_3] \rightleftharpoons \square - \text{MAO} - \square + \text{AlMe}_3 \quad \text{(c)}$$

Fig. 1. (a) Equilibrium involving ‘associated’ and ‘free’ TMA; (b) disproportionation reaction of MAO by TMA; and (c) equilibrium involving ‘associated’ and ‘free’ TMA proposed by Zakharov.

atmosphere. The product was suspended in a solution of MAO (25 mmol of MAO and 20 ml of toluene) and reacted at room temperature for 1 h. This suspension was washed four times with 20 ml of toluene and then 0.1 mmol of $Ni(acac)_2$ was added. After a contact of 5 min, the suspension was thoroughly washed with toluene as described earlier and dried at 40 °C under nitrogen atmosphere.

2.3. Polymerization procedure

The polymerizations were carried out at nitrogen atmosphere in a Schlenk flask (100 ml) at controlled temperature. The reagents were added in the following order: toluene, MAO and catalyst. After 5 min of aging, styrene was added. After the polymerization reaction time elapsed, a solution of ethanol/HCl 5% (v/v) was added in order to deactivate the catalyst system. The polymer was precipitated, washed with ethanol and dried at 60 °C.

2.4. Characterizations

Spectra of ^{13}C NMR were recorded on a Varian Mercury equipment (75 MHz) by using a polystyrene solution in $CDCl_3$. Thermal analyses were performed on Perkin–Elmer DSC7 differential scanning calorimeter; a heating rate of 10 °C/min was used. Molecular weights (M_w and M_n) and polydispersity (M_w/M_n) were measured on Waters *plus* 150CV gel permeation chromatograph, using trichlorobenzene as solvent. The Ni content adsorbed on SiO_2/MAO surface was determined by atomic absorption spectrometry (AAS).

3. Results and discussion

Prior to this study, an attempt to polymerize styrene by using $Ni(acac)_2$ or MAO alone was made. Due to reaction conditions, no polymer was obtained for both cases. This result showed that MAO is indispensable for $Ni(acac)_2$ activation for styrene polymerization.

It is well-known that trimetylaluminum (TMA) always remains together with MAO due to the equilibrium stage between ‘free’ TMA and ‘associated’ TMA (Fig. 1(a)) [27]. Tritto and coworkers [27] have proposed that free TMA might have an important role on the disproportion reaction of MAO producing MAO chains with lower molecular weight (Fig. 1(b)). More recently, Zakharov and coworkers [28] reported that the MAO interaction with free TMA could produce MAO species containing Al with more acidity that acts as an effective cocatalyst during the alkylation process. The equilibrium reaction shown in Fig. 1(c) was dislocated to the right when the molecular weight of MAO increased, accelerating the formation of active species for polymerization.

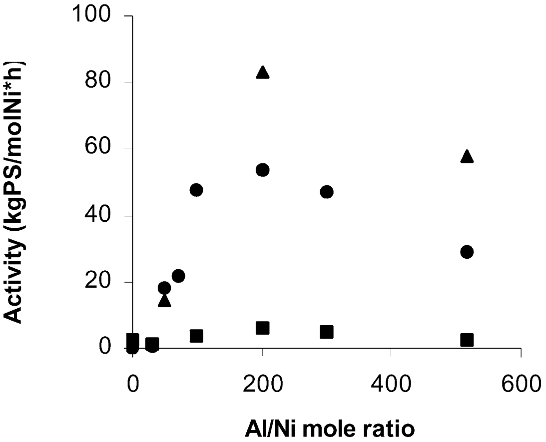


Fig. 2. Activity of catalyst systems versus Al/Ni mole ratio. Reaction conditions: temperature = 40 °C; polymerization time = 24h; [styrene] = 2.15 mol/L; $[Ni(acac)_2] = 10^{-4}$ mol/L; ● = homogeneous system [MAO (Witco)] – System A; ▲ = heterogeneous system [MAO (Akzo)] – System B; ■ = heterogeneous system [MAO (Witco)] – System C.

Fig. 2 shows that catalyst performance depends on MAO molecular weight used on Systems B and C. It was observed that System B has shown the highest activity when compared to System C. This behavior could be attributed to lower contents of TMA in MAO (Akzo). In all catalyst systems, the catalyst activity reached a maximum at Al/Ni = 200 after which it fell off. This behavior could be attributed to an increase in the active species concentration until Al/Ni = 200. Later on the active species concentration decreased due to over-reduction reactions producing Ni(0) species which are not active [17]. In addition, the supported catalyst presented a low activity without MAO as cocatalyst, indicating that the same active species could have been present on silica surface.

In Table 1 for System A, it was observed that molecular weight, isotactic triad and polydispersity were unaffected by Al/Ni mole ratio. Based on the first-order Markov model [29], it was noted that the persistence ratios (ρ) were near to B^{-1} (inverse of Bernoullian parameter). This result suggests that the control of monomer insertion is due to the stereochemistry of growing chain ends. For System C, spectra of ^{13}C NMR have indicated that the microstructures were also unaffected by Al/Ni mole ratio. The values of persistence ratio (ρ) were again almost near to the values of B^{-1}. It was also noted that the polydispersity became

Table 1
Influence of Al/Ni mole ratio on polystyrene microstructure obtained by homogeneous and heterogeneous systems (Reaction conditions: reaction temperature = 40 °C; polymerization time = 24 h; [styrene] = 2.15 mol/l; $[\mathrm{Ni(acac)_2}] = 10^{-4}$ mol/l; nd = not determined; $B = [mr/(2mm + mr)] + [mr/(2rr + mr)]$; $\rho = 2[m][r]/[mr]$)

Al/Ni mole ratio	*mm* (%)	*mr* (%)	*rr* (%)	B^{-1}	ρ	M_w (10^{-4})	M_n (10^{-4})	M_w/M_n
Homogeneous catalyst activated by MAO (Witco)—System A								
50	50	45	5	0.8	0.7	4.1	1.7	2.4
100	50	45	5	0.8	0.7	3.9	1.6	2.4
200	49	45	6	0.8	0.7	nd	nd	nd
300	48	47	5	0.8	0.6	3.8	1.6	2.4
Heterogeneous catalyst activated by MAO (Witco)—System C								
100	25	59	16	0.8	0.7	19.2	2.4	8.0
200	37	50	13	0.9	0.8	23.9	12.0	2.0
300	26	60	14	0.8	0.6	30.6	20.0	1.5
Heterogeneous catalyst activated by MAO (Akzo)—System B								
50	55	36	9	1.1	1.2	49.0	3.6	13.4
200	47	51	2	0.8	0.4	6.5	3.5	1.8
500	nd	nd	nd	nd	nd	8.1	1.8	4.4

narrower when the Al/Ni mole ratio increased. These results could be explained by the presence of multiples active sites at low Al/Ni mole ratio, which produce polystyrene with low molecular weight and broad polydispersity. On the other hand, when the concentration of MAO (Akzo) was increased, the molecular weight decreased substantially. It seems that MAO (Akzo) is more efficient as chain transfer agent than MAO (Witco).

At Al/Ni = 50, System A has produced polystyrene which T_m could not be detected. This polymer has presented 15% of isotactic pentad (*mmmm*) and 35% of pentad (*mmmr*). On the other hand, a completely atactic polymer was produced by System C under the same conditions. Polymer with $T_m = 219$ °C, 55% of isotactic pentad (*mmmm*) and no *mmmr* pentad was obtained by the System B. This superior stereospecificity control of System B might be due to the lower TMA content of MAO (Akzo) than that of MAO (Witco) [15]. This catalyst system produced polymers with isotactic triad, which decreased when Al/Ni mole ratio increased. Hence, high Al/Ni ratios activated catalyst sites with low stereospecific control. These results were confirmed by ρ which is one half of B^{-1} at Al/Ni = 200.

The polymer end-chain structure was analyzed by ^{13}C NMR spectra to elucidate the reaction mechanism. The low molecular weight polymer obtained at Al/Ni mole ratio = 300 was chosen because it is not possible to detect chain-end structures in higher polymers.

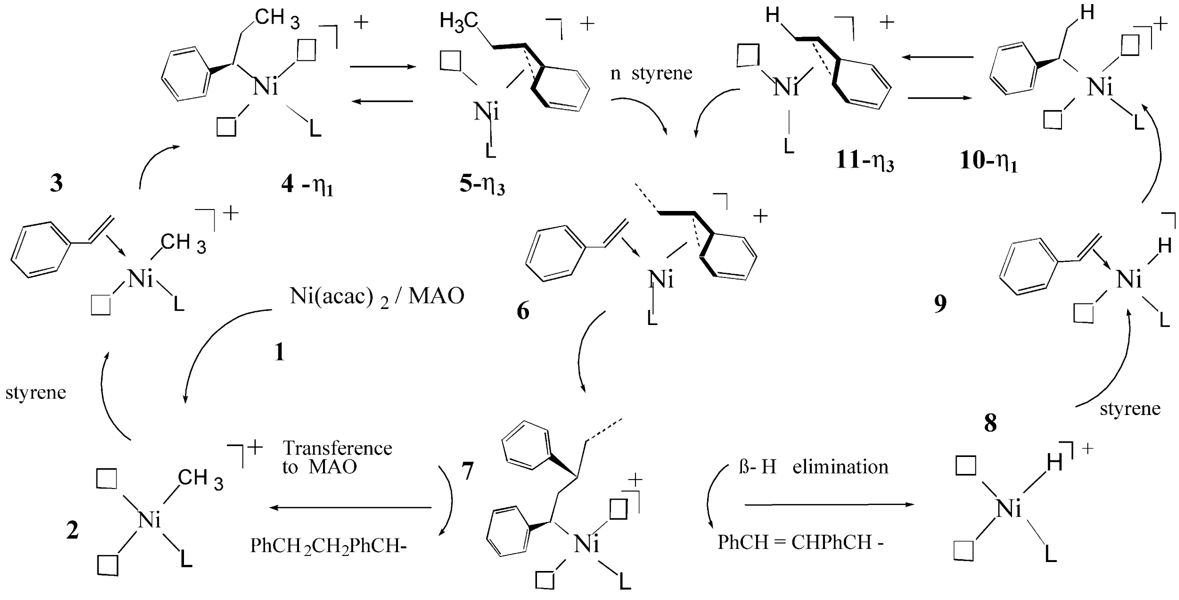
Table 2
Chemical shifts of polystyrene chain-end structures obtained by homogeneous system (Calculated chemical shifts are in parentheses)

Chain-end	^{1}C (ppm)	^{2}C (ppm)	^{3}C (ppm)
$-\mathrm{PhCH{-}CH_2{-}Ph^1CH{-}^2CH_3}$	(37.23) *Eritro*: 37.12 *Treo*: 36.73	(22.43) *Eritro*: 20.96 *Treo*: 21.24	
$-\mathrm{CH{-}Ph^1CH{-}^2CH{=}Ph^3CH}$	(38.7)	(133.49) 134.72	(128.23) 128.59
$-\mathrm{CH_2{-}Ph^1CH{-}^2CH_2{-}Ph^3CH_2}$	(42.45)	(36.56)	(33.57)
$-\mathrm{CH_2{-}PhCH{-}Ph^1CH{=}^2CH_2}$	(143.00)	(113.70)	
$-\mathrm{Ph^1CH{-}^2CH_2{-}^3CH_3}$	(47.61)	(29.78)	(12.12)

Table 2 shows several peaks at aromatic and aliphatic regions of the ^{13}C NMR spectra. Five types of end-chain structure reveal degrees of likelihood and two possible styrene insertions occur at Ni–H and $\mathrm{Ni{-}CH_3}$ bonds. The chemical shifts at aliphatic regions (47.61; 29.78 and 12.12 ppm) and (42.45; 36.56 and 33.57 ppm) are not present. Therefore, $-\mathrm{Ph^1CH{-}^2CH_2{-}^3CH_3}$ and $-\mathrm{CH_2{-}Ph^1CH{-}^2CH_2{-}Ph^3CH_2}$ chain-end groups do not occur at significant amounts. Resonances in aromatic region at 143 and 113.7 ppm were not assigned; consequently, this result shows that the 1,2 insertion did not occur with the last monomer unit. Two close peaks are present in the methyne region at 37.12 and 36.73 ppm and two others in methyl region at 20.96 and 21.24 ppm. They arose from the same end-group, which could assume *erythro* and *threo* configurations.

A polymerization mechanism was proposed by taking the detailed ^{13}C NMR study and the works of Longo [7], Porri [9], Ascenso [31–33] into account. Fig. 3 shows the equilibrium between η_1 and η_3 species. Probably, η_3 determines the styrene insertion into the polymer chain. Ni–η_3 benzyl group is chiral and it can be considered conformationally rigid in the short time between successive insertion steps. In this figure, the main chain termination reaction is β-H elimination producing the chain-end group ($-\mathrm{CH_2{-}PhCH{-}Ph^1CH{=}^2CH_2}$). 2,1-monomer insertion occurs predominantly at Ni–H bond forming the chain-end group ($-\mathrm{Ph^1CH{-}^2CH_3}$). This kind of insertion is necessary in order to form η_3 specie.

Fig. 4 shows the influence of polymerization temperature on the activity of Systems A and B at two reaction times (namely, 2 and 24 h). At 24 h, the activity reached a maximum at 40 °C and then fell off. Probably, the decrease in activity is due to over-reduction reactions at high



L = ligant (styrene, toluene or acetylacetonate); Ph– phenyl; □ = vacant orbital

Fig. 3. Polymerization mechanism for homogeneous catalytic system.

temperatures. On the other hand, System B was slightly affected by polymerization temperature within 2 h.

Table 3 shows that the polymer molecular weight obtained by System B was strongly affected by the reaction temperature. At 50 °C, it produced polystyrene with the highest molecular weight and narrowest molecular weight distribution. Generally, the molecular weight of polymer increases with lowering the polymerization temperature due to significant decrease in the chain transfer rate. However, the lower molecular weight polystyrene was obtained around 30 °C rather than at 50 °C. This tendency could be explained by the more effective decrease of propagation rate at 30 °C. The isotaticity of polystyrene increased while the temperature changed from 40 to 26 °C. At low temperature, $\eta_1 \rightleftharpoons \eta_3$ isomerization (Fig. 3) took place prior to monomer insertion while at high temperature the rate of these processes attained the same order of magnitude. It decreased the isotactic sequence on the polystyrene chain.

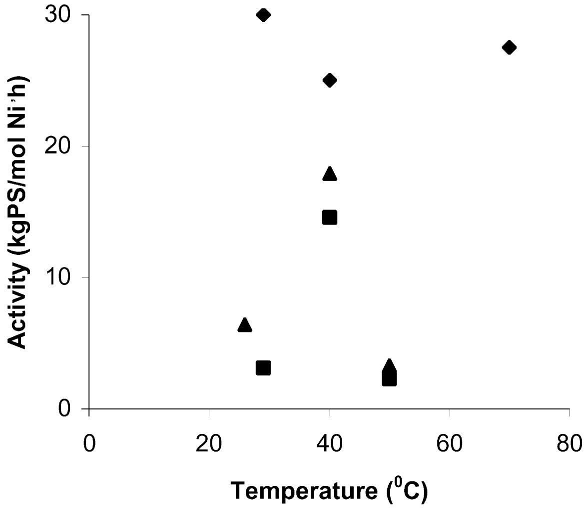


Fig. 4. Activity of catalyst systems versus temperature. Reaction conditions: polymerization time = 24h; $[ni(acac)_2] = 10^{-4}$ mol/L; [styrene] = 2.15 mol/L; Al/Ni mole ration = 50; ▲ = homogeneous system [MAO (Witco)] – System A; ■ = heterogeneous system [MAO (Akro)], System B with polymerization time = 24h; ◆ = heterogeneous system system [MAO (Akzo)], System B with polymerization time = 2h.

Table 4 shows the influence of catalyst concentration on catalyst activity of homogeneous (System D) and heterogeneous (System B) catalysts. The activity reached a maximum at 10^{-4} mol/l. At higher concentration, bimolecular deactivation could have caused the decrease in catalytic activity. It was observed that System D produced polystyrene with high molecular weight when the catalyst concentration decreased. This result could be explained by the dilution effect, which favored the ions pair dissociation. It increased the rate of chain propagation over chain termination. This dilution effect also decreased the bimolecular termination. On the other hand, the polymer molecular weight obtained with System B increased when the catalyst concentration increased. This behavior could be attributed to a higher MAO amount which maintained the Al/Ni mole ratio = 50. Hence, this condition could bring forward active species producing polymers with narrow polydispersity.

Fig. 5 shows the activity versus polymerization time. The activity of System B was higher than that of the homogeneous one. This result was also observed by others authors [18,20,24]. It suggests that the bimolecular deactivation usually observed in homogeneous catalyst is inhibited by

Table 3
Polymerization temperature effects on homogeneous and heterogeneous systems and polystyrene characteristics (Reaction conditions: polymerization time = 24 h; $[Ni(acac)_2] = 10^{-4}$ mol/l; [styrene] = 2.15 mol/l; homogenous [MAO (Witco)]-System A and heterogeneous [MAO (Akzo)]-System B; Al/Ni mole ratio = 50; nd = not determined)

Catalytic system	Temperature (°C)	*mm* (%)	*mr* (%)	*rr* (%)	M_w (10^{-4})	M_w/M_n
$Ni(acac)_2$/MAO system A	26	56	43	1	nd	nd
	40	50	45	5	3.9	2.4
	50	nd	nd	nd	nd	nd
$Ni(acac)_2/MAO/SiO_2$ system B	29	65	34	1	70	16.1
	40	55	36	9	49	13.4
	50	nd	nd	nd	320	5.7

Table 4
Influence of catalyst concentration in activity, polydispersity and polymer molecular weight (Reaction conditions: polymerization time = 24 h; $[Ni(acac)_2] = 10^{-4}$ mol/l; [styrene] = 2.15 mol/l; Al/Ni mole ratio = 50; MAO (Akzo); homogenous catalyst [MAO (Akzo)]-System D and heterogeneous catalyst [MAO (Akzo)]-System B; nd = not determined)

Catalytic system	Concentration (10^4 mol/l)	Activity (kg PS/mol Ni. h)	M_w (10^{-4})	M_w/M_n
$Ni(acac)_2$/MAO system D	0.5	2.08	40	12.3
	1.0	20.83	8.9	1.9
	2.0	1.35	8.2	2.6
$Ni(acac)_2/MAO/SiO_2$ system B	0.5	3.75	nd	nd
	1.0	14.58	49	13.4
	2.0	1.77	146.2	4.0

site isolation effect in the SiO_2/MAO-supported catalyst system.

It was observed that System A catalyst activity increased when polymerization time also increased, but in the time range of 2–4 h the activity was unaffected. This behavior could be explained by the induction time. However, System B activity decreased when polymerization time increased. This result could be attributed to active site deactivation. In addition, the aging time caused a decrease of catalyst activity. This result might be due to deactivation reactions. Babich and coworkers [30] have formerly reported results about chemisorption of $Ni(acac)_2$ on the silica surface. They have reported that one acetilacetonate ligand in the initial $Ni(acac)_2$ undergoes substitution for the hydroxyl group present on the silica surface. Similar reaction of $Ni(acac)_2$ and MAO on the silica surface could also explain the decrease in activity as aging time increased.

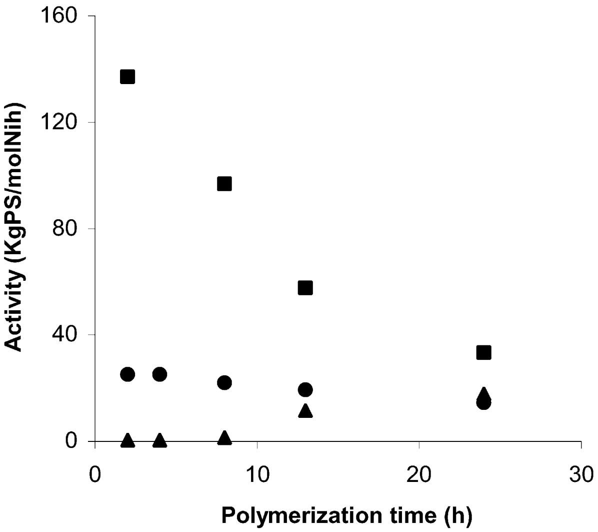


Fig. 5. Catalytic activity versus polymerization time. Polymerization condition: Temperature = 40 °C; $[Ni(acac)_2] = 10^{-4}$ mol/L; [styrene] = 2.15 mol/L; Al/Ni mole ratio = 50; ▲ = homogeneous system [MAO (Witco)] – System A; ■ = heterogeneous system [MAO (Akzo)], System B without aging timer; ● = heterogeneous system [MAO (Akzo)], System B with aging time.

After aging time, System B activity decreased slightly when polymerization time increases. On the other hand, an opposite behavior was observed on the ageless catalyst probably due to the presence of less stable active species. These catalyst species were deactivated during the aging time. Hence, the remaining species were more stable and did not deactivate with polymerization time. Further detailed study is in progress to investigate the nature of active sites species on this supported catalyst system.

4. Conclusion

The $Ni(acac)_2$ and $Ni(acac)_2/MAO/SiO_2$ were active for styrene polymerization combined with MAO as cocatalyst. The catalyst performance and polymer characteristics were dependent upon the parameters reactions and MAO type. It was observed that the heterogeneous catalyst system was more active than the homogeneous one. As also described in literature, evidences were found which suggested that

$\eta_1 \rightleftharpoons \eta_3$ isomerization influences the stereospecificity of homogeneous catalyst. The styrene insertion took place as 2,1-insertion on Ni–H bond formed by β-H elimination.

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