Copolymerization of styrene and methyl methacrylate with nickel acetylacetonate/methylaluminoxane catalyst system

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Abstract

The present work deals with copolymerization of styrene (STY) and methyl methacrylate (MMA) catalysed by nickel acetylacetonate - Ni(acac)$_2$, employing methylaluminoxane (MAO) as cocatalyst. This catalyst system presented low catalyst activities for STY homopolymerization and very high activities for MMA. It seems that the catalyst system based on Ni(acac)$_2$/MAO is effective for the copolymerization of MMA and STY to give block copolymer but it also produced polystyrene and poly(methyl methacrylate) homopolymers. The polymers were characterized by ^{13}C NMR, GPC and FTIR. The polystyrene homopolymer was identified by IR and NMR analyses of the cyclohexane soluble fraction. The presence of absorption bands correspondent to carbonyl group and aromatic ring was observed in the IR spectrum of the acetic acid soluble part. This result is a clue that STY-MMA copolymer with low molecular weight was produced. The high molecular weight copolymer (acetic acid insoluble fraction) was also characterized by IR analysis which indicated the presence of characteristic absorption bands of carbonyl group and aromatic ring. These results were confirmed by ^{13}C NMR analysis.

Introduction

It has been reported that the catalyst system based on Ni(acac)$_2$ activated by MAO is effective for the STY polymerization (1-4). According to some of these works, it is possible to obtain polystyrene with different kinds of tacticity (atactic, isotactic or syndiotactic). On the other hand, Ni(acac)$_2$ combined with MAO is also effective for MMA polymerization (5-7).

Over the last two years, we have been interested in polymerizing polar monomers with transition metal based catalysts. We have already studied catalyst systems for homopolymerizations of MMA and STY using transition metal catalysts activated by MAO (5,8-11) and we have presented some results about copolymerizations of these monomers (10). In those former papers, the preliminary results were reported on the homopolymerization of MMA, vinylpyridine and STY, which have pointed out many interesting features of the polar monomers.

Thus, the aim of this work was the investigation of MMA and STY copolymerization employing the binary catalyst system based on Ni(acac)$_2$/MAO.

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Experimental part

Materials

Ni(acac)$_2$ (TCI, Japan) was purified by azeotropic distillation. MAO (30 wt% toluene suspension) supplied by Witco GmbH was used without further purification. STY (donated by Nitriflex S.A.) and MMA (donated by Metacril S.A.) were distilled over calcium hydride. Solvents were purified under nitrogen by conventional methods.

Polymerization procedure

The polymerizations were carried out under dry nitrogen atmosphere in a 100 mL Schlenk flask equipped with a magnetic stirrer. Fresh toluene (recently distilled)(30 mL), methylaluminoxane in toluene suspension (3 mmol) and Ni(acac)$_2$ in toluene solution (0.03 mmol) were injected into the flask in that order, using syringes. The polymerization was started by adding a determined amount of STY at 35 °C. After 30 minutes, determined amount of MMA was added and the polymerization was let to progress for 5 minutes more and then it was quenched by 5% HCl methanol solution. The polymer was washed with methanol and dried at 60 °C. Polymer yields were calculated by gravimetry.

Kinetic experiments

The polymerizations of MMA and STY were conducted at 35°C using mechanical stirrer in 250 mL of toluene with 15.0 mmol of MAO, 0.15 mmol of Ni(acac)$_2$ and 0.235 mol of monomer. In predetermined times, aliquots of 2 mL were taken and conversion was determined by gravimetry.
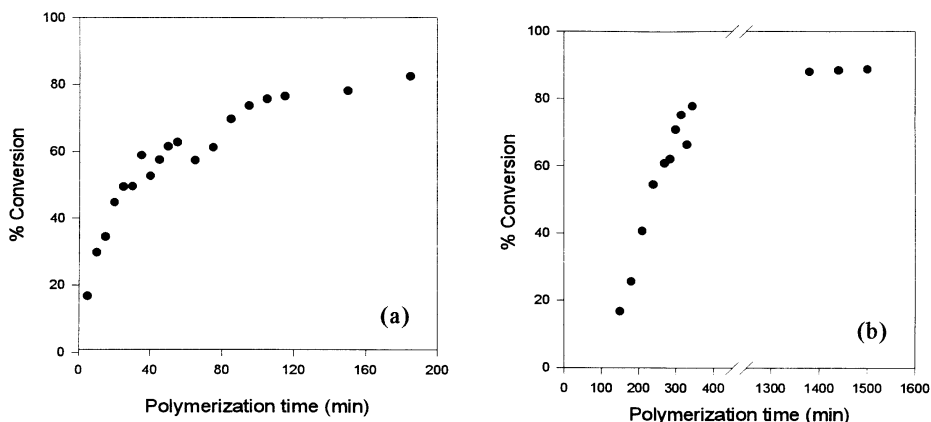
Polymer characterization

The molecular weight and molecular weight distribution were measured by GPC (Waters 150C *Plus*) at room temperature using chloroform as solvent and calibrated with standard polystyrene columns. The copolymer composition was measured by IR (Perkin Elmer 1720x) using the relative intensities of carbonyl absorption band (1720 cm^{-1}). The ^{13}C NMR spectra were recorded on a Varian VXR-300 FT-NMR spectrometer operating at 75,4 MHz. The polymer solutions were prepared by dissolving ca. 50 mg of polymer in 0.5 mL. CDCl$_3$.

Results and discussion

Homopolymerizations of MMA and STY were carried out in order to investigate their kinetic behaviour with the catalyst system based on Ni(acac)$_2$/MAO. Figure 1 shows the conversion curves of both homopolymerizations. As it can be seen the catalyst was more active for MMA than STY. Literature points an interaction between MMA and MAO by complex formation (6,7,12), thus the higher activity for MMA can be attributed to this complex formation. In addition, it is also possible that MMA changes the coordination sphere of nickel by removing the acetylacetonate group.

From the former data, copolymerizations of MMA and STY were conducted using different STY/MMA mole ratios. It was observed that after addition of all catalyst components, the color of the solution changed from light green to dark brown, indicating the alkylation of Ni compound by MAO. STY was kept to react during 30 min due to its low reactivity with this catalyst system and after that period a determined amount of MMA was added to the reactor. It was noted that after the addition of STY, the catalyst system became lighter brown, indicating na interaction among the components of the mixture.

Figure 1 - Conversion curves of methyl methacrylate (a) and styrene (b) homo-polymerization

Three fractions were separated. The first one was isolated by cyclohexane extraction and was characterized as polystyrene homopolymer (SCH). The cyclohexane insoluble fraction was submitted to acetic acid extraction to remove poly(methyl methacrylate) homopolymer (SAA). The acetic acid insoluble (IAA) fraction was considered to be the MMA-STY copolymer.

Figure 2 shows that higher yield was achieved when a higher amount of MMA was used. This can be attributed to the higher reactivity of MMA with this catalyst system. Figure 3 (a, b and c) shows that the increase of MMA amount on the feed provoked an increase of the SAA fraction (Figure 3b) and a decrease of the SCH fraction (Figure 3a) and also a decrease of the IAA fraction (Figure 3c). These results can also be attributed to the higher reactivity of MMA when compared to STY.

The IR analysis of the SCH fraction has confirmed it to be polystyrene. Its molecular weight (Mw) was low and molecular weight distribution was narrow, as seen in Table 1. These results suggest that the propagation proceeds by only one type of coordinative active center, as shown by Crossetti (13).

The IR spectra of the SAA fraction displayed characteristic bands of the carbonyl group (ester) and aromatic ring. GPC curves of these polymers were bimodal and showed that the molecular weights were low (Mw $\cong 10^4$). These results may indicate the presence of homopolymer of poly(methyl methacrylate) and low molecular weight copolymer of MMA and STY.

The IR spectra of the IAA fraction displayed bands corresponding to the carbonyl group (ester) and aromatic ring, indicating that the catalyst system may have produced a copolymer of MMA and STY. The composition of these fractions was estimated by infrared spectrometry by the absorption band of ester carbonyl group (at 1720 cm^{-1}). Figure 4 shows that copolymer composition of the IAA fraction changes as the amount of MMA in the polymerization feed is varied. It can be seen that the incorporation of MMA remains almost constant until 50% of MMA in polymerization feed. The MMA contents determined by NMR analysis were slightly higher than those determined by IR analysis. The GPC curves showed that high molecular weight (Mw ???10^5) bimodal polymers were produced. Figure 5 exhibits a typical ^{13}C NMR spectrum of a polymer (IAA fraction)

Figure 2 - Conversion *versus* amount of methyl methacrylate in comonomer feed

% molar methyl methacrylate in comonomer feed

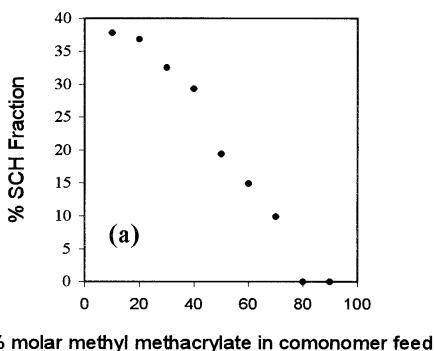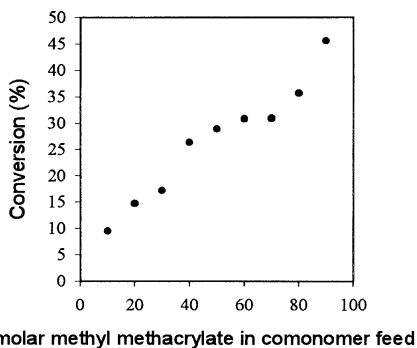% molar methyl methacrylate in comonomer feed

Figure 3 - Influence of amount of methyl methacrylate in the comonomer feed in the SCH fraction (a), SAA fraction (b) and IAA fraction (c)
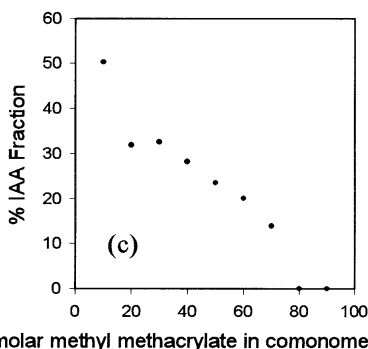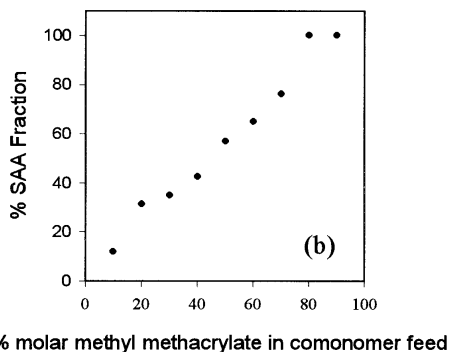

% molar methyl methacrylate in comonomer feed

% molar methyl methacrylate in comonomer feed

Table 1 - Results of GPC analysis of SCH fraction

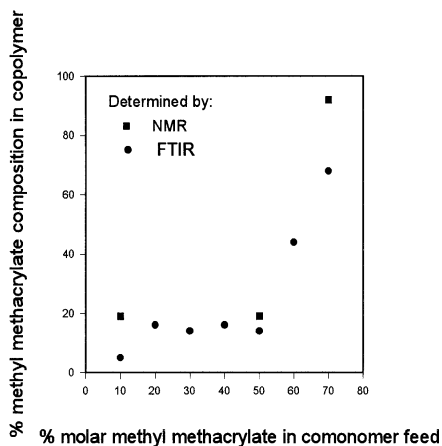| MMA in the comonomer feed (% molar)	Mw x 10^{-4}	Mw/Mn
10	4.09	1.3
20	4.59	1.3
30	3.12	2.0
50	3.27	1.9

Figure 4 - Curve of MMA composition in the copolymer *versus* MMA amount in the polymerization feed

Table 2 - Triads distribution of styrene (STY) and methylmethacrylate (MMA) sequences in the copolymer (IAA fraction)

MMA in comonomer feed (% molar)	STY sequence (%)			MMA sequence (%)		
	mm	mr	rr	mm	mr	rr
10	57	18	25	20	22	58
50	58	26	16	9	16	75
70	-	-	-	11	17	72

Figure 5 - Typical ^{13}C NMR spectrum of copolymer obtained with 50% MMA in the polymerization feed
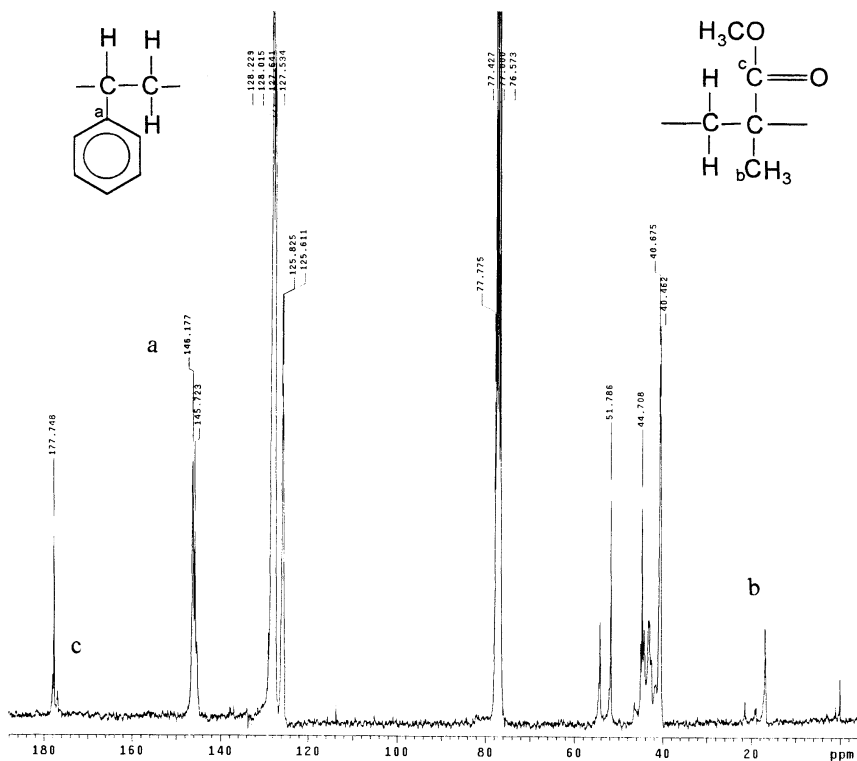
obtained from 50 mole % MMA in the comonomer feed. It shows the shift of aromatic ring of STY (from 145.7 to 145.2 ppm), carbonyl and methyl group of MMA (177.7 and 16-22 ppm, respectively). As can be seen in Table 2, stereoregular polystyrene, which is insoluble in acetic acid and cyclohexane, was not produced. In addition, comparing our ^{13}C NMR spectrum data with results from the literature (14,15), we may conclude that these copolymers were neither alternating nor statistical STY-MMA copolymers. Thus, these results suggest that the copolymers are block-like although to our knowledge, there is no literature data available for the assignments of these block copolymers. Based on the results presented in this work, we can also conclude that the IAA fraction was not a mixture of homopolymers.

References

1) Ishihara N, Kuramoto M, Uoi M (1988) *Macromolecules* **21**: 3356

2) Longo L, Grassi A, Oliva L, Ammendola P (1990) *Makromol Chem* **191**: 237

3) Endo K, Masaki K (1994) *Kobunshi Ronbunshu* **51(10)**: 652; *Chem. Abstr.* **121**, 281314j (1994)

4) Crossetti GL, Bormioli C, Ripa A, Giarrusso A, Porri L (1997) *Macromol Rapid Commun.,* **18**:801

5) Coutinho FMB, Costa MAS, Monteiro LF, de Santa Maria L.C. (1997) *Polym Bull,* **38**: 308

6) Endo K, Inukai A, Otsu T (1994) *Macromol Rapid Commun,* **15**:893

7) Endo K, Inukai A, Otsu T (1995) *Makromol Chem Phys* **196**: 2065

8) Coutinho FMB, Dias ML, Monteiro LF, de Santa Maria LC - *PAT'95,* Proceedings of the *Third International Symposium on Polymer for Advanced Technologies,* Pisa/Italy, 152, 1995.

9) Coutinho FMB, LC de Santa Maria, Dias ML, Gonçalves MCM - Proceedings of the *Fourth Pacific Polymer Conference,* Kauai/Hawaii/USA, 163, 1995.

10) Coutinho FMB, Monteiro LF, Costa MAS, de Santa Maria LC - Proceedings of the *VII International Macromolecular Colloquium,* Gramado/RS/Brazil, 44, 1996.

11) Dias ML, Bruno MI, de Santa Maria LC (1997) *Eur Polym J,* **33**: 1559

12) Reddy SS, Shashidhar G, Sivaram S (1993) *Macromolecules* **26**: 2132

13) Crossetti GL - PhD Thesis, *Polimerizzazionee dello stirene e del butadiene con il sistema MAO-Ni(acac)$_2$,* Politecnico diMilano (1996)

14) Aerdts AM, de Haan JW, German AL, van der Velden GPM (1991) *Macromolecules* **24**: 1473

15) Aerdts AM, de Haan JW, German AL (1993) *Macromolecules,* **26**: 1965