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Methylaluminoxane: only a cocatalyst or something more?

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Summary

Methylaluminoxane (MAO) was used as a catalyst for the polymerization of several vinyl monomers. Polymer yields were found to decrease in the order styrene > isobutyl vinyl ether > methyl methacrylate ≈ acrylonitrile > α-methylstyrene > vinyl acetate = 0. The polymers exhibit low to moderate molar mass with broad distributions. NMR analysis were used to determine the polymers steric microstructure and the end groups. MAO was also able to produce styrene-methyl methacrylate, styrene-isobutyl vinyl ether and methyl methacrylate-isobutyl vinyl ether copolymers. Experimental evidences are against ionic polymerization mechanisms, whereas proofs for a radical mechanism are more controversial, but altogether against of it.

Introduction

Methylaluminoxane (MAO) is the key component of many catalytic systems for the polymerization of ethylene [1-5], α-olefins [1-5], styrene [1,2,6,7], dienes [3,7] and polar monomers [2,8]. Since its discovery [9] MAO (and other aluminoxanes as well) were widely studied with the aim to define the chemical structure and to understand its role in the catalytically active species formation when combined with transition-metal compounds [10]. In spite of this, MAO structure is in part still unclear and many aspects at the basis of these mechanisms are not yet explained; several authors address MAO as a “black-box”. Moreover many different “MAO” actually exist, depending on how they are prepared.

MAO is used to activate the transition-metal compounds and to generate the alkylated metal cation responsible of coordinated polymerization. However, the literature often neglects the fact that in some cases MAO itself is able to polymerize monomers without the involvment of any other metal compound. This is the origin, for instance, of the atactic polstyrene formed as a by-product in the syndiospecific polymerization of styrene with titanium/MAO systems [6]. Such behavior is not entirely surprising, considering the ability of metaloxanes-related derivatives (of aluminum, zinc and other metals) to initiate the polymerization of several kind of monomers, including styrenes [11-13], acrylates [14-15], lactones [14,16-19] epoxides [12,20,21].

As for unsaturated monomers polymerization with alkylaluminoxanes, a few authors put forward some hypothesis on the active species involved and on the polymerization mechanism. Saegusa [11] reported the polymerization of styrene, α-methylstyrene and isobutyl vinyl ether with $AlEt_3$/water/acyl or alkyl halide systems, forming aluminoxanes species in situ. The authors proposed a mechanism in which ethylaluminoxane (or $AlEt_3$) behaves as Lewis acid, forming a carbonium ion complex with the organic halide cocatalyst which initiates the polymerization. Sivaram [15] used methylaluminoxane containing different amounts of residual $AlMe_3$ to initiate the photopolymerization of methyl methacrylate (MMA). A radical mechanism is proposed, involving the formation of a complex between the monomer and the $AlMe_3$ present in MAO, in which this residual $AlMe_3$ would be the true initiating species.

Reporting the homo- and copolymerization of styrene-methyl acrylate with Ti-MAO systems, Cunningham [22-23] observed traces of poly(methyl acrylate) in blank runs. An anionic mechanism is suggested as the possible cause.

More in general, it is known that alkylaluminum initiators bearing polydentate ligands containing nitrogen or oxygen (that in some way can be assimilated to MAO) are catalysts for the polymerization of unsaturated monomers like olefins [24,25] and methacrylates [25,26]. These initiators are active in cationic form, whereas the polymerization does not proceed when they are in the neutral form [26]. In all cases the authors agree that the reaction mechanism and the real identity of the active species are not known. It is even proposed that the mechanism is monomer-dependent: cationic for isobutylene [25], group-transfer-like for MMA [25,26], or one not yet understood for ethylene [24,25,27,28] (possibly an insertion mechanism).

Summarizing, aluminoxanes have been considered cationic [11], radical [15] and anionic [14] initiators, but as a matter of fact the nature of the active species involved in their reactions is still debated and pretty unclear [29]. In a previous report, we advanced the hypotesis that MAO could generate a zwitterion [30]; the so formed (acidic) ionic centers would coordinate the monomer double bond, eventually leading to polymerization.

The aim of this work is to report some results about the catalytic activity of MAO, aluminum alkyls and their mixtures in the polymerization of styrene. Reactions with other unsaturated monomers bearing electron-actracting or -donating groups were also performed. Hopefully, such results bring a contribution for further studies.

Experimental

Materials

Styrene (EniChem) was stirred overnight over calcium hydride and purified by filtration on a basic alumina bed (Fluka, type 5016 A) or distillation under reduced pressure; acrylonitrile (Aldrich) and methyl methacrylate were distilled over calcium hydride in nitrogen atmosphere; isobutyl vinyl ether (Aldrich) was distilled over sodium in nitrogen atmosphere.

Methylaluminoxane (either Crompton Co., 10% in toluene or Aldrich, 9.5% in toluene) was used either as received or after solvent distillation and drying at 60°C under vacuum for 2 hours. MAO samples were named MAOc (commercial MAO from Crompton Co.), MAOa (commercial MAO from Aldrich) and MAOd (MAOc treated under vacuum). MAOc contains 34.9-35.8% of trimethylaluminum, according to the supplier's certificate of analysis. Tetraisobutyldialuminoxane, 20% in heptane

(TIBAO; Crompton Co.), trimethylaluminum, 2 M in toluene (TMA; Aldrich) and triisobutylaluminum, 1 M in toluene (TIBA; Aldrich) were used as received.
Sulfur and 2,2,6,6-tetramethylpiperidinyl-1-oxyl (Aldrich) were used as received.

Polymerization Runs

Polymerizations were performed in bulk under nitrogen atmosphere in Schlenk tubes, adding the proper amount of catalyst(s) to the monomer (typically 5-10 mL) and stirring the reaction at the selected temperature for the required time. The reactions were stopped by adding acidified ethanol and the polymers were precipitated in excess alcohol, filtered and dried under vacuum at 60°C.

Characterization

Nuclear Magnetic Resonance (NMR): ^{13}C-NMR spectra were recorded at 110°C on a Bruker Avance 400 spectrometer operating at a frequency of 100.62 MHz.
Gel Permeation Chromatography (GPC): mass-average molar masses were measured by GPC with a Waters 600 chromatograph in tetrahydrofuran. Narrow molar mass distribution polystyrene standards were used for calibration.
Infrared analysis (IR): IR spectra were collected with a FT-IR Nicolet Nexus spectrometer in the 4800-400 cm^{-1} range with 64 scans at a resolution of 2 cm^{-1}. All the samples were analysed in transmission as KBr disks. In order to determine the % mol of styrene units in the raw products, calibration curves were obtained measuring the relative intensity of the 1600 cm^{-1} styrene unit band with respect to the 1387 cm^{-1} MMA methyl band for a series of PS-PMMA blends of different composition.

Results and discussion

Polymerization of styrene

Styrene polymerization was carried out in bulk with different aluminum compounds, at constant monomer/aluminum ratio. A blank run gave no polymeric product (Table 1, first entry), demonstrating that thermal self-polymerization is absent under the adopted experimental conditions. Aluminum alkyls, such as triisobutylaluminum or trimethylaluminum, were poor polymerization initiators: TIBA was inactive, whereas TMA afforded only traces of polystyrene.
Among the tested compounds, commercial methylaluminoxane, MAOc, was the most active. The reaction reproducibility was acceptable: yields of 10.3, 12.4 and 14.6% were obtained in three different runs (only the last run is reported in Table 1). Mass-average molar mass (Mw) is rather low (34000 Da), much lower than the typical values found in radical or syndiospecific polymerization, suggesting that chain-transfer and/or termination processes are very relevant for the reaction pathway. Worth to note, the polystyrene afforded by TMA has a much higher molar mass.
Under similar conditions, during the syndiospecific polymerization of styrene with the $CpTiCl_3$/MAOc catalytic system (60°C, [styrene]/[titanium]=28000, [Al]/[Ti]=1200 and [styrene]/[Al]=23.3), comparable amounts of atactic polystyrene by-product (11.2%) are formed besides syndiotactic polystyrene [31]. Molar masses of this atactic polystyrene and those formed by MAO alone are also comparable.

Table 1 – Polymerization of styrene with aluminum alkyls and aluminoxanes (T = 60°C, t = 2 h unless otherwise indicated)

catalyst	[Styrene]/[MAO]	[Styrene]/[Al]	yield (wt %)	Mw[a] (10^3)
none	-	-	0	-
TMA	-	23	0.3	153
TIBA	-	23	0	-
MAOc	23	23	14.6	34
MAOc	23	23	17.0[b]	n.d.
MAOa	23	23	4.2	30
MAOa	23	23	13.0[c]	43
MAOc + TMA (2:1)	35	23	4.6	25
MAOc + TIBA (2:1)	35	23	2.0	n.d.
MAOd	23	23	2.4	40
MAOd + TMA (1:1)	46	23	3.0	47
MAOd + TIBA (1:1)	46	23	6.5	27
TIBAO	-	23	0.04	n.d.

[a] n.d. = not determined; [b] reaction temperature = 90°C; [c] reaction time = 8 h

Commercial MAO always contains “free” TMA, generally one third of the total aluminum, which cannot be removed completely. The presence of TMA markedly affects the behavior of metallocenes/MAO system [15,31-35]. Campbell et al. found that TMA can be lowered to less than 10% by treatment of the commercial solution at 70°C under vacuum [36]; activity and selectivity in styrene syndiospecific polymerization and the polymer molar mass are greatly enhanced after this treatment. MAOd was obtained according to a procedure similar to that above described. Accordingly, MAOd is much less active than MAOc in the non-stereospecific polymerization of styrene, affording only 2.4% of polystyrene, also in agreement with previously published data [37]. MAOa, which contains a lower amount of structural TMA (~22% vs. ~35%), is less active than MAOc.

The addition of either TMA or TIBA to MAOc led to a significant decrease of conversion, suggesting that aluminum alkyls either do not partecipate to the polymerization (in such case the decrease of conversion would be an effect of the dilution of MAO in the reaction mixture) or partially disrupt MAO structure.

The back addition of TMA or TIBA to MAOd increased the yields, but did not restore the activity up to the levels of MAOc. With TIBA, the yield increase was higher; with TMA, almost negligible. It is known from the literature that the back addition of TMA to thermally-treated MAO leads to disproportionation phenomena that imply a decrease of molar mass [32]; clearly, in the present case the thermal treatment to get rid of the “free” trimethylaluminum actually caused an irreversible change in MAO structure, also removing some structural trimethylaluminum that was not restored by the successive back addition. Finally, the fact that tetraisobutyldialuminoxane only afforded small traces of polymer could be viewed as a consequence of the lower Lewis acidity as compared to MAO; very likely the basic monomer double bond must interact with the acid centers of aluminoxane to be activated and to start the polymerization, the higher the acidity, the stronger the interaction.

Radical inhibitors were added to the polymerization mixture to study their effect and try to establish if the polymerizaton mechanism could be radical. Since hindered phenols cannot be employed for this purpose, because the acidic hydrogen would react with MAO, elemental sulfur or TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl radical) at different concentrations were used. The yield was not affected by these inhibitors (an increase above 30% was even observed at [Al]/[TEMPO]=5). Carrying out some comparative tests, also in the presence of a radical initiator (AIBN), it was found that TEMPO reacts with aluminum alkyls, possibly because of some redox process that transforms it into another species [38] removing the unpaired radical. The same conclusion was reached recently from other authors [39]. A similar lack of inhibition was observed with elemental sulfur: in this case the characteristic smell suggests the formation of a mercaptan derivative. In conclusion, the method to add radical inhibitors to the reaction medium cannot be used to establish if the mechanism is radical or not, because they react with the TMA contained in MAO.

To investigate the possible ionic nature of the propagating species, attempts to trap the growing chain with either electrophilic (carbon dioxide) or nucleophilic (2,6-di-tert-butylphenol, triphenylphosphine) species were made. The polymer end-groups were analyzed by ^{13}C-NMR, but no traces of end-functionalized chains were detected in any case. The lack of these chains is likely the consequence of the non-livingness of the propagating species. Indeed, by plotting the number-average molar mass versus reaction times (Figure 1), Mn values do not increase, as would be expected for a living process (on the contrary, they even decrease). Besides, the shape of the curve in Figure 1, with a yield limited well below ~25% suggests that the catalyst undergoes a slow dectivaction with time.

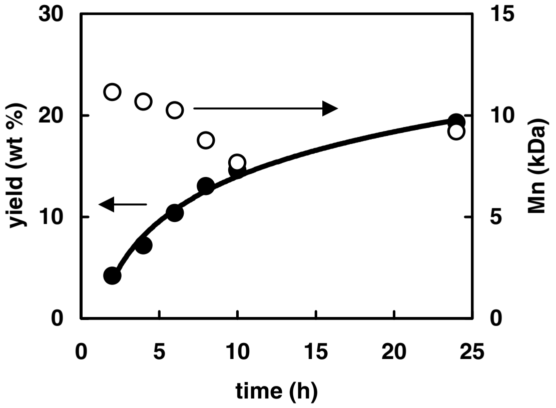
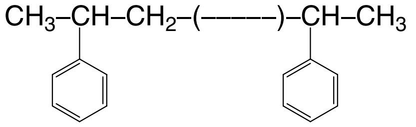


Figure 1. Conversion (●) and number-average molar mass (O) vs. time in the polymerization of styrene with MAOa. T = 60°C; [styrene]/[MAOa] = 23.

The analysis of the end groups showed that unsaturated bonds are absent, excluding that the termination of the polymer chain proceeds through H-elimination. CH_3-CH(Ph)-- groups are the most abundant, but also CH_3-CH_2-CH(Ph)-- groups are present in low concentration, in a ratio approx. 1:9. This would be in agreement with a mechanism where the polymer chains are formally initiated by a CH_3 of MAO (whatever is the nature of this methyl group) attacking the PhCH= carbon of styrene; as an alternative, a primary insertion of a styrene molecule in the CH_3-Al bond could take place.



In both cases the result would be a polymer chain with the structure sketched above. Worth to note, if the reaction proceeds through an attack to the PhCH= carbon, the propagating group would be a $--CH_2^*$ (whatever the nature of the "asterisk"), and this does not appear very convincing, leaving the insertion mechanism as a reasonable alternative. On the other hand, CH_3-CH_2-CH(Ph)--, the minor component, would derive either by attack on the CH_2= carbon of styrene or a secondary insertion; both these possibilities are sound.

Polymerization of other unsaturated monomers

To gather more information on the mechanism, we studied the polymerization behavior of monomers other than styrene. In fact, the vinyl monomers reactivity depends on the nature of the substituent on the double bond [40,41]: vinyl ethers (e.g. isobutyl vinyl ether) are not able to undergo anionic polymerization, whereas acrylic monomers (e.g. methyl methacrylate, acrylonitrile) cannot be polymerized with cationic initiators. The results are reported in Table 2. All the mentioned monomers afforded the corresponding polymers, with the remarkable exception of vinyl acetate which is a monomer known to polymerize only *via* a radical mechanism [42]. α-methylstyrene, which usually exhibits high propagation rates in cationic polymerizations [41], gave only traces of polymer.

Table 2 - Polymerization of unsaturated monomers with MAO (t= 8 h)

monomer	catalyst	[monomer]/[MAO]	T (°C)	yield (wt %)	Mw[a] (10^3)	Mw/Mn
styrene	MAOa	23	60	13.0	43	4.8
methylmethacrylate	MAOa	23	60	3.3	94[b]	2.0
isobutyl vinyl ether	MAOa	23	60	9.7	9[c]	2.4
vinyl acetate	MAOa	23	60	0	-	-
α-methylstyrene	MAOa	23	60	0.5	n.d.	n.d.
styrene	MAOc	100	25	2.6	n.d.	n.d.
acrylonitrile	MAOc	100	25	2.1	n.d.	n.d.
methyl methacrylate	MAOc	100	25	2.0	n.d.	n.d.
isobutyl vinyl ether	MAOc	100	25	5.1	n.d.	n.d.
vinyl acetate	MAOc	100	25	0	-	-

[a] n.d. = not determined; [b] THF-soluble fraction; [c] contains also a low-molar mass fraction

Poly(methyl methacrylate) (PMMA) was partially insoluble and contained a small percentage of crosslinked units. These units (3÷5% of the total methacrylate) consists of carboxylate groups, presumably deriving from the cleavage of $–COOCH_3$ functionalities, bridged intermolecularly by $Al(OH)^{++}$ ions, as shown by IR analysis.

Addition of cationic inhibitors (pyridine or 2,6-di-t-butylpyridine) to the polymerization of IBVE did not change neither the conversion, nor the molar mass of the products. All the findings seem in disagreement with a supposedly ionic character of the propagating chain. As for a radical propagating chain, the medium-to-low molar masses, the lack of formation of poly(vinyl acetate) and the smooth formation of poly(isobutyl vinyl ether), are hints against this mechanism.

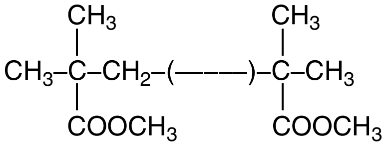
Table 3 - Steric microstructure of PS, PMMA and PIBVE determined by ^{13}C-NMR

polymer	MAO-catalyzed polymerization			radical polymerization		
	mm	mr	rr	mm	mr	rr
PS	32	56	12	21	59	20
PMMA	3[a]	35[a]	62[a]	3	34	63
PIBVE	31	41	28	19	42	39

[a] tetrachloroethane-soluble fraction

The steric structure of the obtained polymers is reported in Table 3 and compared with that of radical polymers (initiator: AIBN at 60°C). While MAO-catalyzed PMMA microstructure is the same of a radical PMMA, PS and PIBVE obtained with MAO are more isotactic than the corresponding radical polymers.

NMR analysis gave also information on the end-groups. The most abundant terminals in PMMA (at least, in its tetrachloroethane soluble fraction) are $(CH_3)_2(CH_3OOC)C$--, in analogy to PS.



$$CH_3-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-(\text{———})-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_3$$

In the case of PMMA also a small portion of unsaturated groups $CH_2=C(COOCH_3)$-- is found in the polymer, whose formation does not have at the moment a straight explanation. Also, it must be remarked that ethyl end-groups, which would derive from the attack of a methyl of MAO to the methylene group of MMA [23], are absent in the NMR spectrum (10 ppm region). Again, a primary insertion of the monomer in the CH_3-Al bond could account for the experimental observation.

Copolymerizations

Copolymerizations of the three binary mixtures of styrene, isobutyl vinyl ether and methyl methacrylate are reported in Table 4. The raw polymers were fractionated and the resulting fractions were examined by NMR (when possible) and IR spectroscopies. The P(S-IBVE) copolymer (soluble in heptane) has a blocky structure and contains about 80% of styrene units, as shown by its NMR spectrum. As for the MMA-IBVE system, because IBVE units were found in the ethyl ether-insoluble fraction, it is deduced that a copolymer is formed, possibly along PMMA homopolymer; however, the crosslinking makes impossible to obtain further structural data and to draw any other conclusion. Similar considerations are valid for the S-MMA system; in this case the formation of a copolymer is demonstrated by the presence of styrene units (almost 40%) in the cyclohexane-insoluble fraction. Therefore, the formation of true copolymers is certain in all cases, and the presence of different polymeric species, is an indication that MAO behaves as a multisite catalyst.

Table 4 - Copolymerization results (equimolar monomer feeds, [monomers]/[MAO]= 25, T = 60°C, t = 24 h)

monomers	yield (wt%)	solvent for fractionation	soluble fraction	insoluble fraction
S-IBVE	3.4	n-heptane	(~95%) P(S-IBVE)	(~5%) PS
MMA-IBVE	5.5	ethyl ether	(~75%) PIBVE	(~25%) PMMA (?) P(MMA-IBVE)[a]
S-MMA	14.7	hot cyclohexane	(~15%) PS	(~85%) PMMA (?) P(S-MMA)[a]

[a] The insoluble fraction contains Al and may consist also of crosslinked (co)polymer

The styrene-methyl methacrylate system was studied in greater detail for feed compositions in the range 10-90% (Table 5). The polymer yield increases with the amount of styrene in the feed. The compositions of the raw copolymers were determined by IR analysis, due to the insolubility of the products. The incorporation of styrene units was always under 45% in spite of the feed composition. Since the raw polymers are in principle blends of PS, PMMA and copolymer - both linear and crosslinked - these percentages are only rough indications of the real copolymer compositions and must be considered with caution (but, worth to note, the 50:50 copolymer maintained substantially the same composition *after* extraction of PS). The low styrene content and the probable azeotropic behavior, are features different from those arising from any known mechanism [43].

Table 5 - Copolymerization of styrene and MMA ([monomers]/[MAO]= 25, T = 60°C, t=24 h)

Styrene in the feed (mol%)	10	20	30	40	50	60	70	80	90
Yield (wt%)	9.2	11.1	11.0	14.4	14.7	17.3	20.0	21.0	20.2
Styrene units in the raw product (mol%)[a]	16	24	29	38	37	41	42	42	43

[a] ± 10%

Conclusion

MAO is able to catalyze the homo- and copolymerization of a variety of vinyl monomers. Styrene and vinyl monomers bearing either electron-rich (IBVE) or -poor (AN, MMA) substituents give the corresponding polymers, exhibiting low to moderate molar masses and broad distributions; PMMA and its copolymers are partially crosslinked. The characteristics of the obtained (co)polymers do not fit with those determined for any previously reported mechanism (radical, anionic, cationic).

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