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Methylaluminoxane/haloalkane as initiator system for styrene polymerization

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Summary

Styrene polymerization was initiated by methylaluminoxane in the presence of haloalkane. The propagating species are shown by trapping experiments and electron paramagnetic resonance to be both radicals and cations.

Introduction

Recently, monocyclopentadienyl titanium complexes activated with methylaluminoxane (MAO) had been found to catalyze syndiospecific polymerization of styrene (S).[1,2] The dominant syndioselective active species was shown by electron magnetic resonance to be trivalent titanium complexes.[3-5] Electrodialysis polymerizations were performed with the cell arrangement: (+) | CpTi(OR)$_3$, MAO, solvent || MAO, S, solvent |(-) to investigate the ionic nature of the catalytic species. No polymer was found in either compartment at 500V potential when toluene was used as the solvent. Therefore, the catalytic species formed in the anodic compartment has little or no ionic mobility. Changing the solvent to organic halogen compound to increase the medium dielectric constant resulted in the production of atactic polystyrene (*a*-PS) in the cathodic compartment. The yield of *a*-PS is low for chlorinated benzenes and high for haloalkanes. An unexpected observation was that formation of *a*-PS was not affected by the electric field, the same yield was produced with or without it. In other words, the initiating species does not contain the monocyclopentadienyl titanium compound and the MAO/RX system itself is an efficient initiator for stereo-random polymerization of S.

Experimental

Procedures for the synthesis of CpTi(OR)$_3$ and MAO, purification of monomer and solvent, polymerization of S, and separation of PS into syndiotactic and atactic fractions have been given in detail previously.[3-5] The yield of *s*-PS (SY) is the fraction of the polymer insoluble in refluxing 2-butanone, the balance is the soluble, amorphous *a*-PS.

Results and Discussion

$CpTi(OPh)_3$/MAO is a very active syndiospecific catalyst for styrene polymerization[4] producing high yields of *s*-PS (Table I exp. 12). Changing the solvent to *o*-dichlorobenzene (DCB) caused an increase in the aspecific polymerization to form more *a*-PS. In the absence of $CpTi(OPh)_3$, MAO alone in DCB produce a little *a*-PS and no *s*-PS (exp. 16). However, MAO in 1,1-dichloroethane (DCE) solvent, with or without $CpTi(OPh)_3$, initiated rapid polymerization of styrene to produce only *a*-PS (exp. 17-19). Therefore, MAO/DCE is an efficient initiator system for non-stereoselective styrene polymerization.

Table I Results of styrene polymerization[a]

Exp.	Solvent[b] (50 ml)	[Ti][c] (μM)	[MAO] (mM)	Yield Total (g)	Yield *s*-PS (%)	T_m (°C)	T_g (°C)
12	T	50	100	1.2	98	260	96
14	T/DCB[d]	50	100	1.24	84		
15	DCB	50	100	1.4	66		
16	DCB	0	100	0.09			
17	T/DCE[d]	50	100	2.44	0	none	85
18	DCE	50	100	3.75	0	none	80
19	DCE	0	100	3.74	0	none	80

[a]Polymerization of 5 mL of S in 50 ml of solvent for 30 min at room temperature; [b] solvent: T = toluene, DCB = *o*-dichlorobenzene, DCE = CH_3CHCl_2; [c]Ti = $CpTi(OPh)_3$; [d]solvent mixture 1:1 by volume.

The effects of reagents which trap radicals and cations were investigated since styrene is readily polymerized by both species. In the experiments below the trap reagent was first introduced into a Schlenk tube then MAO (0.029 g, 0.5 mmol), S (5 mL) and CH_3CHCl_2 (45 mL) were added. These operations were performed inside a Vacuum Atmosphere dry box. This mixture, in the absence of any trapping agent, produced about 3.2-3.8 g of *a*-PS in 30 min at 30°C. The addition of 5,5-dimethyl-1-pyrrolinoxyl (0.0283 g, 0.25 mmol) inhibited completely any styrene polymerization. When *t*-butylphenyl nitrone (9 mg, [Al]/[nitrone] = 10) was introduced, the formation of *a*-PS was reduced to 9 mg, which is about 0.3% of the yield in the absence of nitrone. A series of styrene polymerizations were initiated by 2 mmol of MAO; 2.5 min later various amount of nitrone was added. The polymerizations were stopped at the end of 30 min. The yield of *a*-PS was 0.4, 0.41, 0.54, 0.61 and 2.4 g for [nitrone]/[Al] ratio of 0.1, 0.05, 0.02, 0.01 and 0, respectively.

A solution of MAO (0.5 mmol, 0.06 M), dichloroethane (12.7 mmol, 1.52 M), nitrone (0.5 mmol) in toluene (7 mL) produced a characteristic triplet electron paramagnetic resonance spectra of nitroxide radical (g = 2.009, ^{N}a = 14.6 G). The integrated intensity of the spectra represents 5.8 μM of radicals corresponding to $[\gtrsim NO\bullet]/[Al] = 10^{-4}$. This shows that free radicals are formed by the reaction of MAO with CH_3CHCl_2.

The role of cation in MAO/RX initiated styrene polymerization was also examined. NaN_3 was finely grounded and dried in vacuo for 1 h. In exp. 96, 0.29 g of MAO was mixed with different amount of NaN_3 (a) 30 mg, (b) 6 mg, (c) 3 mg corresponding to $[Al]/[N_3^-]$ = 1, 5 and 10, respectively. Then 50 mL of CH_3CHCl_2 and 5 mL of styrene were added to each Schlenk tube. No polymer was produced in all these cases. NaN_3 was also added after certain time of styrene polymerization (t_p) had transpired. In exp. 100, (Table II), eight polymerizations were carried out using MAO (2 mmol), S (5 mL), and dichloroethane (45 mL), and T_p = 25°C. At t_p = 2 min. different amounts of NaN_3, corresponding to $[Al]/[N_3^-]$ from 2 to 2,500 were added. The *a*-PS yield after a total

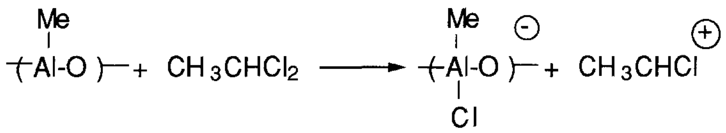
Table II Effect of N_3^- on styrene polymerization[a]

Exp. 100		Exp. 90			Exp. 91		
MAO/S/DCE(N_3^- added at t_p = 2 min)		CpTi(OPh3)/MAO/S/T (N_3^- added at t_p=6 min)			CpTi(OPh)3/MAO/S/DCB (N_3^- added at t_p=6 min)		
$[N_3^-]/[Al]$	Yield of *a*-PS (g)	$[N_3^-]$ [Ti]	Yield (g)	SY (%)	$[N_3^-]$ [Ti]	Yield (g)	SY (%)
0	3.78	0	0.85	98.0	0	1.2	82
0.0004	1.9	0.1	0.77	99.5	0.1	1.1	87
0.001	1.3	0.3	0.78	99.4	0.3	1.1	86
0.002	0.78	0.7	0.58	99.6	0.7	1.1	88
0.01	0.84				1	0.83	89
0.05	0.80				3	0.86	89
0.25	0.75						
0.5	0.73						

t_p of 30 min. decreased from 3.78 g with no N_3^- to 0.73 g for $[Al]/[N_3^-] = 2$. These experiments suggest that the initial reaction products between MAO and DCE are cations which were all scavenged by N_3^-. The cations react further to form species not traped by N_3^- such as free radicals.

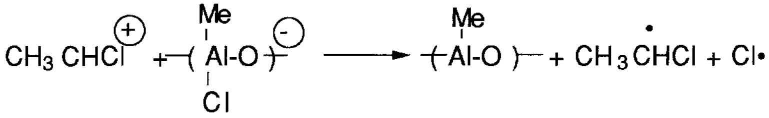
The extent of cation involvement in styrene polymerization by the $CpTi(OPh)_3$/MAO catalyst was investigated. In exp. 90, four polymerizations at 50°C were carried out for mixtures of $CpTi(OPh)_3$ (2.5 μmol), MAO (5 mmol), S (3 mL), and toluene (50 mL). At $t_p = 6$ min. different quantity of NaN_3 was added at ratios of $[N_3^-]/[Ti]$ ranging from 0 to 0.7. The yield at $t_p = 30$ min. decreased from 0.85 g without N_3^- to 0.58 g at $[N_3^-][Ti] = 0.7$ (Table II). The presence of N_3^- lowered the yield of PS but raised SY to 99.6%. This suggests the participation of cations in this system and that the cations may be scavenged by N_3^-. In exp. 91, which contained DCE, different amount of NaN_3 was introduced after 6 min. and polymerization continued for 24 min more. The total yield of PS was greater but SY smaller in these experiments than in exp. 90. These results suggest that while there may be cationic catalytic species in the $CpTi(OR)_3$/MAO initiated syndiospecific styrene polymerization (exp. 90), they are minor in comparison to the dominant propagating species from MAO/RX.

The results described above indicate the formation of both free radical and cationic initiating species from MAO/CH_3CHCl_2. We may postulate that MAO reacts with CH_3CHCl_2 to first form ionic species by

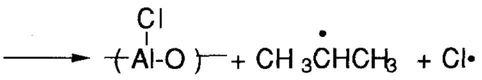


$$-\!\left(\overset{\text{Me}}{\text{Al}}\text{-O}\right)\!- + CH_3CHCl_2 \longrightarrow -\!\left(\underset{\text{Cl}}{\overset{\text{Me}}{\text{Al}}}\text{-O}\right)^{\ominus}\!- + CH_3CHCl^{\oplus} \qquad (1)$$

This initiates cationic polymerization of styrene which can be inhibited by N_3^-. Neutralization of cation can produce radicals to initiate styrene polymerization which was inihibited by dimethylpyrrolinoxyl and nitrone. The nitrone trapped nitroxyl was observed by EPR. The nature of the reactions which produced the radicals is not known, some possible processes may be,



$$CH_3CHCl^{\oplus} + -\!\left(\underset{\text{Cl}}{\overset{\text{Me}}{\text{Al}}}\text{-O}\right)^{\ominus}\!- \longrightarrow -\!\left(\overset{\text{Me}}{\text{Al}}\text{-O}\right)\!- + CH_3\dot{C}HCl + Cl\bullet \qquad (2)$$



$$\longrightarrow -\!\left(\overset{\text{Cl}}{\text{Al}}\text{-O}\right)\!- + CH_3\dot{C}HCH_3 + Cl\bullet \qquad (3)$$

which leads to free radical polymerization of S.

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