

SOME PRELIMINARY INFORMATION ON SYNDIOTACTIC POLYSTYRENE CATALYSTS

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ABSTRACT

Syndiotactic specific polymerization of styrene has been investigated by ^{13}C NMR analysis and isotopic labelling methods. The value of the activation energy involved in the steric control has been determined. Some information of the number of the active sites and on the life of the catalysts is reported.

Syndiotactic polymerization of styrene, in the presence of titanium or zirconium compounds and methylaluminoxane was recently reported in the literature^[1,2]. A variety of titanium compounds, such as titanium tetrabutoxide^[3], tetrabenzyltitanium^[2], titanium triacetylacetonate^[3], cyclopentadienyltitanium trichloride^[4] are suitable for promoting syndiotactic polymerization.

Table 1 shows the results of a series of polymerization runs carried out in the presence of tetrabenzyltitanium and methylaluminoxane at 40°C, at increasing reaction times. The amount of polymer produced increases linearly with reaction time, suggesting that the catalytic complexes are

Table 1 Results of the polymerization runs
stopped with ^3H labelled butanol.

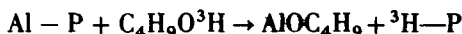
Run	Time (min)	Yield (mg)	Radioactivity (cpm/mg)	Incorporated ^3H (mol $\times 10^6$)	$[\eta]$
1	20	62	457	0.45	0.21
2	40	173	499	1.4	0.41
3	60	248	731	2.9	0.49
4	80	382	502	3.0	0.56
5	100	426	446	3.0	0.56

Polymerization conditions; toluene 20 ml, styrene 20 ml, methylaluminoxane 5.2×10^{-3} mol (based on Al), tetrabenzyltitanium 3.4×10^{-5} mol. $T=40^\circ\text{C}$. All the polymerization runs have been stopped by injecting 2 ml of OH tritiated n-butanol with activity of 6.3×10^{10} cpm/mol.

stable in the reaction conditions. The intrinsic viscosity also increases approaching an asymptotic value, after 80 minutes.

This fact suggests that chain propagation rate is not very high and that in these conditions chain transfer processes are not so relevant as they are at higher polymerization temperature^[5]. Stereoregularity of the polymer is always very close to 100% syndiotacticity (see e. g. Fig. 1-a).

When polymerizations are terminated by addition of butanol OH labelled with ^3H , some radioactivity is detected on the polymer samples. The total amount of ^3H incorporated on the whole polymer reaches a steady value after a short polymerization time (see Table I). This fact suggests that chain transfer with aluminoxane is irrelevant if any. In fact chain transfer with organoaluminum compounds would lead to an amount of aluminum-polymer bonds increasing with polymerization time and consequently to an increasing amount of ^3H in the polymer, resulting from butanolysis of the aluminum-polymer bonds:



Therefore, considering that most probably the incorporation of ^3H comes from butanolysis of the titanium-carbon bonds between the growing polymer chains and the titanium atoms of the catalytic complexes, and that the limit amount of the incorporated ^3H is approximately 10% of the amount of tetrabenzyltitanium introduced in the reactor at the beginning of the polymerization one would conclude that, in our conditions (if the isotopic effect is disregarded), about 10% of the titanium present in the system is involved in the catalysis.

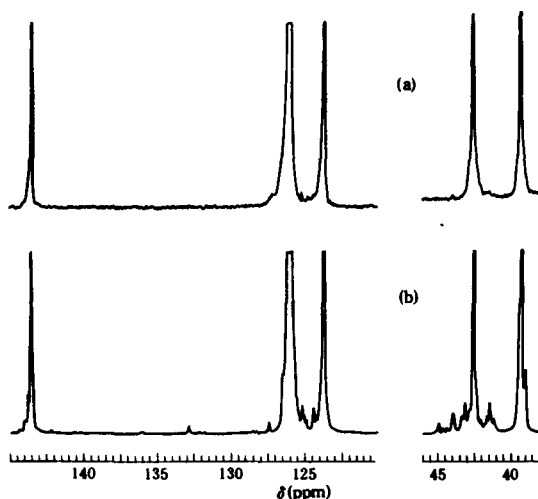


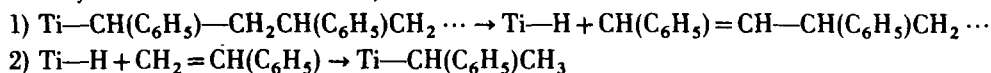
Fig. 1(a) ^1H decoupled ^{13}C NMR spectrum of a polystyrene sample prepared at 50°C with tetrabenzyltitanium and methylaluminoxane. HMDS scale.

(b) ^1H decoupled ^{13}C NMR spectrum of a polystyrene sample prepared at 50°C with tetrabenzylzirconium and methylaluminoxane. HMDS scale.

In both spectra the main resonances are due respectively to quaternary aromatic carbon (143.5 ppm), ortho and meta aromatic carbons (125.9 ppm), para aromatic carbons (123.6 ppm), aliphatic methylene carbons (42.4 ppm) and methine carbons (39.2 ppm).

It is worth mentioning that, in a previous paper^[5] dealing with the NMR investigation of the end groups of low molecular weight polymers, prepared at higher temperature it was shown that the

most important chain transfer process involves β hydrogen abstraction and initiation of new polymer chains on the resulting Ti—H bonds, according to the following equations (notice the secondary insertion of the monomer):



As shown in Fig. 1—a polystyrene obtained in the presence of tetrabenzyltitanium is almost completely syndiotactic. Even performing polymerization at higher temperature (e. g. at 100°C) the amount of stereo sequences other than rrr remains negligible. Less stereoregular polymers may be obtained by using zirconium based catalysts, such as tetrabenzyl-zirconium, and methylaluminoxane^[2].

In fact in the ¹³C NMR spectrum of a sample of polystyrene obtained at 50°C in the presence of the just mentioned catalysts, one can appreciate the presence of stereosequences in addition to the rrr methylene tetrads (see Fig. 1-b). As previously reported^[2], the distribution of the different stereosequences of the considered polymers is in agreement with the Bernoullian symmetric statistical model proposed by Bovey^[6]. By ¹³C NMR analysis one can evaluate P_r and $P_m (= 1 - P_r)$ for different polymerization temperatures (see Table 2 and Experimental Part) and the driving force of the syndiotactic steric control in the presence of zirconium catalysts, by means of the equation (see

Table 2 Stereospecificity of styrene polymerization at different temperatures

Run	T(K)	Time (min)	Yield (g)	P_r
6	313	180	0.25	0.940
7	333	195	1.90	0.935
8	353	120	2.48	0.930
9	373	80	2.51	0.920
10	393	60	2.05	0.910

Polymerization conditions: solvent (toluene for runs 6—9, xylene for run 10) 20 ml, styrene 20ml, methylaluminoxane 5.2×10^{-3} mol (based on Al), tetrabenzylzirconium 3.7×10^{-5} mol. P_r were determined as described in Expl. Part.

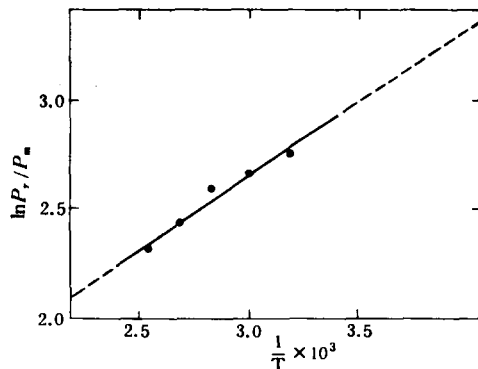


Fig. 2 Arrhenius plot of the stereoregularity of syndiotactic polystyrene samples obtained in runs 6—10 (see Table 2), plotted according to equation $\ln P_r / P_m = a_r / a_m + (E_m - E_r) / R \cdot 1/T$. The difference $E_m - E_r$, evaluated from the slope of the experimental straight line, is 1.3 Kcal/mol.

Fig. 2) previously proposed for syndiotactic polymerization of propene^[7].

$$\ln \frac{P_r}{P_m} = \ln \frac{a_r}{a_m} + \frac{E_m - E_r}{RT}$$

P_r and P_m are the probabilities of syndiotactic and isotactic placements, respectively, a_m and a_r are the Arrhenius preexponential coefficients, E_r and E_m are the activation energies for the formation of syndiotactic and isotactic dyads, respectively. For zirconium based catalysts, the value determined for the difference $E_m - E_r$ is 1.3 Kcal/mol. Of course the driving force of the syndiotactic steric control is higher for titanium based catalysts.

CONCLUSIONS

From the data reported one can reach at least three conclusions concerning syndiotactic polymerization of styrene.

- 1) The variety of transition metal compounds which can be used for the preparation of the catalysts suggests that the original ligands of the transition metal compounds can be removed in the reaction with methylaluminoxane.
- 2) At least in our conditions, only a fraction of the transition metal is involved in the catalysis.
- 3) Titanium based catalysts are considerably more stereospecific than zirconium based catalysts.

EXPERIMENTAL PART

Materials

Tetrabenzyltitanium and tetrabenzylzirconium were prepared according to the literature^[8]. Methylaluminoxane was prepared as reported^[9] by reaction of $\text{Al}(\text{CH}_3)_3$ with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in toluene; the solvent and the unreacted $\text{Al}(\text{CH}_3)_3$ were removed by distillation under vacuum. Reagent grade styrene was refluxed over calcium hydride and distilled prior to use.

Polymerizations

Anhydrous toluene, methylaluminoxane, styrene and the transition metal compound were introduced in this order under nitrogen atmosphere in a glass flask thermostated with an oil bath and magnetically stirred. Polymerization conditions and results are reported in the tables. Runs 1—5 were stopped by injecting 2 ml of OH tritiated butanol and stirred for 30 min. in order to achieve complete butanolysis of metal-polymeryl bonds; runs 6—10 were stopped by injecting 5 ml of methanol. All the polymers were coagulated in acidified methanol, separated by filtration, washed with methanol and dried under vacuum. Viscosity measurements were performed in *o*-dichlorobenzene at 135°C.

Radioactivity measurements

The radioactivity of polymer samples obtained in runs 1—5 was measured by using a liquid scintillation spectrometer Beckmann LS 8100. All the samples were previously dissolved in toluene and precipitated in methanol twice in order to remove any radioactivity contamination.

A sample of non-tritiated polystyrene was stirred for 30 min. in contact with OH tritiated butanol in the presence of the catalytic system and treated as the previous samples. Its radioactivity

was measured for comparison. The value found was 6.6 cpm/mg.

¹³C NMR analysis

The ¹³C NMR spectra of the polymer samples obtained in runs 6–10 were recorded with a Bruker AM 250 spectrometer operating at 62.89 MHz in the FT mode at 393°K, by using tetrachlorodideuterioethane as solvent and hexamethyldisiloxane (HMDS) as internal reference. The inverse gated mode of recording was used in order to obtain proton-decoupled ¹³C spectra without NOE. The spectra are the result of 8 K transients with 32 K data points with an acquisition time of 1.4 s and a spectral width of 12 KHZ. A pulse width of 3 s, corresponding to a 79° flip angle, and relaxation delay of 7 s were used. All spectra were processed with a 2 HZ line broadening function prior to transformation. The concentration of the stereochemical tetrads has been determined from the areas of the corresponding methylene resonances: rmr 44.4–43.5; rrr 43.4–42.2; mrm 42.2–41.8; rrm 41.8–40.8; mmm 41.1–40.8; mrm 40.7–40.0 ppm. P'_m s and P'_r s have been determined by using the following relationships, proposed by Bovey^[6] for symmetric Bernoullian chain propagation: $[rrr] = P_r^3$; $[rrm] = 2 P_r^2 P_m$; $[rmr] = P_r^2 P_m$; $[mrm] = P_m^2 P_r$; $[mmm] = P_m^3$.

Keywords: Syndiotactic polystyrene; Stereosequence; Activation energy; Active site.

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REFERENCES

- [1] Ishihara, N.; Seimiya, T.; Kuramoto, M. and Uoi, M., *Macromolecules*, **1986**, *19*, 2465.
- [2] Grassi, A.; Pellecchia, C.; Longo, P. and Zambelli, A., *Gazz.Chim. Ital.*, **1987**, *117*, 249.
- [3] Italian Patent Application **1986**, 41007, A86
- [4] Ishihara, N.; Kuramoto, M. and Uoi, M., European Patent Application **1987**, 0210615, Az
- [5] Zambelli, A.; Longo, P.; Pellecchia, C. and Grassi, A., *Macromolecules*, **1987**, *20*, 2037.
- [6] Bovey, F.A. and Tiers, G.V.D., *J.Polym.Sci.*, **1960**, *44*, 173.
- [7] Zambelli, A.; Locatelli, P.; Zannoni, G. and Bovey, F.A., *Macromolecules*, **1978**, *11*, 923.
- [8] Zucchini, V.; Albizzati, E. and Giannini, V., *J. Organomet.Chem.*, **1971**, *26*, 357.
- [9] Ewen, J.A., *J.Am.Chem.Soc.*, **1984**, *106*, 6355.