

HIGHLY ACTIVE CATALYTIC STEREOSPECIFIC POLYMERIZATION OF STYRENE

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ABSTRACT

A novel highly active catalyst of $\text{TiCl}_4/\text{MgCl}_2\text{-Al}(\text{C}_2\text{H}_5)_3$ system (called SN-1 catalyst, in which rare earth compound NdCl_3 is included) was used for studying stereospecific polymerization of styrene in benzene solution. Highly isotactic polystyrene was prepared with far better yield and higher catalytic efficiency than the results ever reported in literatures. The influences of concentration of monomer, catalyst, triethylaluminum as well as polymerization temperature on the catalytic efficiency, yield, tacticity and molecular weight of polystyrene have been investigated.

In 1955 Ziegler^[1] and Natta^[2] had reported the coordination polymerization of styrene giving isotactic polystyrene with $T_g=85\text{--}100^\circ\text{C}$ and $T_m=200\text{--}230^\circ\text{C}$. Since then various catalyst systems^[3-21] of Ti, V, Cr and Zr etc. had been found for synthesis of polystyrene but usually with poor isotacticity, low yield and catalytic efficiency as shown in Table 1. From 7th decade a lot of highly active supported catalysts have been used for synthesis of poly-

Table 1 Styrene stereospecific polymerization with various catalysts

Author	Catalyst system	Solvent	T ($^\circ\text{C}$)	Time (h)	Yield (%)	Cat. eff. (gPS/gTi)	Tacticity
Natta ^[3,4] (1955)	$\text{TiCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$	Benzene	70	7	43.7	38	Cryst.
Williams ^[5] (1958)	$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$	Heptane	70	24	72	51.2	Isotactic
Overberger ^[6] (1959)	$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$	Heptane	80	20	30	11.9	Cryst.
Furukawa ^[7] (1959)	$\text{TiCl}_4\text{-Cd}(\text{C}_2\text{H}_5)_2$	Hexane	80	7	88.5	19.2	Atactic
Kern ^[11] (1963)	$\text{TiCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$	—	50	2-4	8.2 ~13.7	76.9 ~128.2	Cryst.
Otto ^[12] (1964)	$\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$	Benzene	40	4	7.1	41.6	—
Kapur ^[14] (1968)	$\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$	Hexane	40	1	2	7	40% Iso- tactic
Kapur ^[16] (1973)	$\text{Cr}(\text{acac})_3/\text{Al}(\text{i-C}_4\text{H}_9)_3$	Benzene	40	6	10.5	79.8	Atactic
Ballard ^[17] (1973)	$\text{Zr}(\text{CH}_2\text{-C}_6\text{H}_5)_4$	Toluene	30	160	20	38	Atactic
Koide ^[20] (1976)	$\text{TiO-n}(\text{C}_4\text{H}_9)_4\text{-Al}(\text{C}_2\text{H}_5)_3$	Hexane	60	20	24	15.2	—
Мардъкин ^[21] (1981)	$\text{TiCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3 \cdot 1/3\text{Mg}(\text{C}_6\text{H}_{13})_2$	Hexane	70	4	28	51.7	80% Iso- tactic

ethylene and isotactic polypropylene with quite successful achievements, but still no supported catalyst has been reported for stereospecific polymerization of styrene with high isotacticity, good yield as well as catalytic efficiency.

In this laboratory, a novel highly active supported catalyst system of TiCl_4 , $\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{C}_2\text{H}_5)_3$ (called SN-1 catalyst) was prepared for stereospecific polymerization of styrene in benzene solution under atmospheric pressure. Highly isotactic polystyrenes were synthesized with far better yield and higher catalytic efficiency than the results ever reported in literatures. Our typical experimental results are given in Table 2.

Table 2 Stereospecific polymerization of styrene in benzene with highly active supported catalyst SN-1

SN-1 [Ti] (mmol/l)	$[\text{Al}(\text{C}_2\text{H}_5)_3]$ (mmol/l)	[Styrene] (mol/l)	T ($^{\circ}\text{C}$)	Time (h)	Yield (%)	Cat. eff. (gPS/gTi)	i-PS (%)
1.5	14.0	0.48	50	2	47	331	92.9
1.5	14.0	0.96	50	2	64.9	902	98.1
1.5	14.0	1.44	50	2	81.8	1720	98.8
1.5	14.0	1.92	50	2	86.2	2400	95.0
1.5	14.0	2.40	50	2	63	2197	96.2
1.5	14.0	2.88	50	2	51	2082	95.6
1.0	14.0	0.96	50	2	25	527	93.8
1.5	14.0	0.96	50	2	64.9	902	98.1
2.5	14.0	0.96	50	2	97.7	824	97.1
3.0	14.0	0.96	50	2	93	637	94.7
1.5	14.0	0.96	26.5	2	40.7	563	96.0
1.5	14.0	0.96	35	2	45.0	620	96.4
1.5	14.0	0.96	45	2	52.4	527	94.6

The influences of the concentrations of styrene monomer, catalyst, triethylaluminum and of the polymerization temperature on the isotacticity, yield, catalytic efficiency and molecular weight of polystyrene have been investigated.

EXPERIMENTAL

Catalyst preparation

SN-1 supported catalyst composed of TiCl_4 , $\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{C}_2\text{H}_5)_3$ was prepared by co-milling anhydrous MgCl_2 , TiCl_4 with small amount of NdCl_3 and then activated by $\text{Al}(\text{C}_2\text{H}_5)_3$. Preliminary experiments revealed that the catalyst prepared by the same procedure but consisting of metal chloride NdCl_3 only (i.e. no TiCl_4 was added in it) was inactive for styrene polymerization, while the catalyst consisting of only TiCl_4 was active, but the isotactic-

city of polystyrene so obtained was quite low. NdCl_3 in SN-1 catalyst seems to play a role of promoter for raising isotacticity of polystyrene.

Polymerization

Adequate amounts of styrene and SN-1 catalyst were added into 100–150 ml of benzene. Solution polymerization was carried out in a mechanically stirring reactor filled with N_2 atmosphere under ambient pressure for 2 hours. The temperature was controlled by thermostat within $\pm 1^\circ\text{C}$.

Isotacticity determination

About 2g of polymer products were extracted by refluxing with 100 times by weight of butanone-2 for 8 hours. The weight percentage of insoluble fraction was calculated as the isotacticity of polystyrene.

Structural determination

The insoluble fractions in extraction with butanone-2 were taken for characterization by IR, X-D and DSC measurements and were confirmed to be isotactic polystyrene ($T_m = 220^\circ\text{C}$) with coincidence to the literatures.

Molecular weight determination

The following equation^[22] was used for determination of number average molecular weight, $\bar{M}_n$, of isotactic polystyrene by viscosity method:

$$[\eta] = 25.9 \times 10^{-5} \bar{M}_n^{0.734} \text{ (dl/g)}$$

(solvent: CHCl_3 , temperature: 30°C)

RESULTS AND DISCUSSION

1. Yield catalytic efficiency and isotacticity

Monomer concentration: Figure 1 shows the effect of initial concentration of monomer styrene on the yield, catalytic efficiency and isotacticity of polystyrene, obtained by polymerization with SN-1 catalyst under definite condition for 2 hours. On the curves, the peak of yield (i.e., 86%) occurs at $[\text{styrene}]_0 = 20\text{g/dl}$, and the peak of catalytic efficiency (i.e., 2400 gPS/gTi) appears at nearly the same abscissa. The peak value of catalytic efficiency is 20–100 times greater than those reported in literatures (see Table 1). The isotacticities of polystyrene mostly keep above 95% and the maximum value of isotacticity is up to 98.8%. Both of the above experimental data clearly dispaty the specialty of SN-1 catalyst used for stereospecific polymerization of styrene.

When over this starting concentration of styrene monomer, the polymerization mass becomes too sticky for mechanical stirring, that will reduce the rate of polymerization and so depress the yield and catalytic efficiency from the peak value.

Catalyst concentration: As shown in Figure 2, at definite initial concentration of styrene

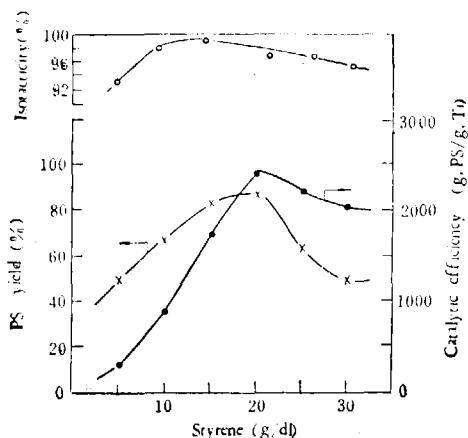


Fig. 1 Correlation of PS Yield, isotacticity and catalytic efficiency with starting styrene concentration

$[Ti] = 1.5 \text{ mmol/l}$; $[Al(C_2H_5)_3] = 14 \text{ mmol/l}$;
Polym. temp.: 50°C ; Polym. time: 2 h.

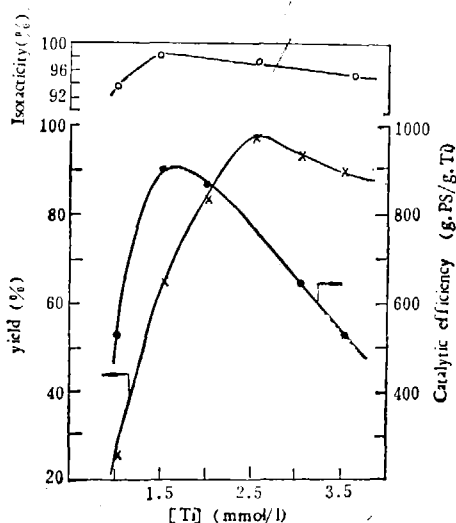


Fig. 2 Correlation of PS yield, isotacticity and catalytic efficiency with catalyst concentration $[Ti]$

$[Styrene] = 0.96 \text{ mol/l}$; $[Al(C_2H_5)_3] = 14 \text{ mmol/l}$;
Sol.: Benzene; Temp.: 50°C ; Time: 2 h.

monomer and triethylaluminum, the yield and catalytic efficiency of styrene polymerization are effected by catalyst concentration. The peak value of yield equals 97.7% at $[Ti] = 2.5 \text{ mmol/l}$ and the peak value of catalytic efficiency equals 902 gPS/gTi at $[Ti] = 1.5 \text{ mmol/l}$.

When $[Ti] > 1.5 \text{ mmol/l}$, the value of catalytic efficiency begins to drop down owing to the increasing yield of polystyrene causing the polymerization mass too sticky for mechanical agitation, therefore retarding the diffusion of monomer molecules toward the active centers of catalyst. Under such condition the catalytic active centers can not perform their function

of chain propagation reaction thoroughly and effectively, and thus the catalytic efficiency is depressed. When $[Ti] > 2.5$ mmol/l, the polymerization mass turns rapidly to sticky-gummy so that the polymerization reaction will soon be retarded thus giving poorer yield of polystyrene.

Triethyl aluminum concentration: By varying concentration of triethylaluminum at definite polymerization condition, the yield and catalytic efficiency are effected as shown in Figure 3. The two corresponding peak values appear at $[Al]/[Ti] = 13.7$ mol/mol. At lower value of $[Al]/[Ti]$, the activation of catalyst would be weakened, and at higher value over-reduction of active centers would occur, and thus the yield and catalytic efficiency would decrease.

Polymerization temperature: Figure 4 shows that the peak values of the yield, catalytic efficiency and isotacticity all appear at polymerization temperature being 50°C . Beneath this

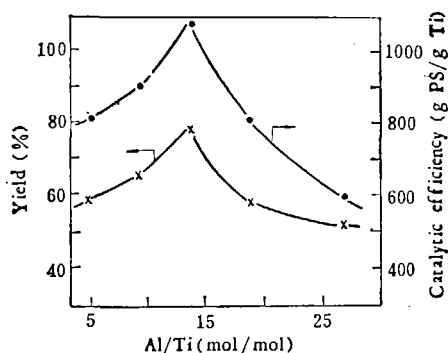


Fig. 3 Correlation of PS yield and catalytic efficiency with molar ratio of Al/Ti
[Styrene] = 10% (g/dl); [Ti] = 1.5 mmol/l.

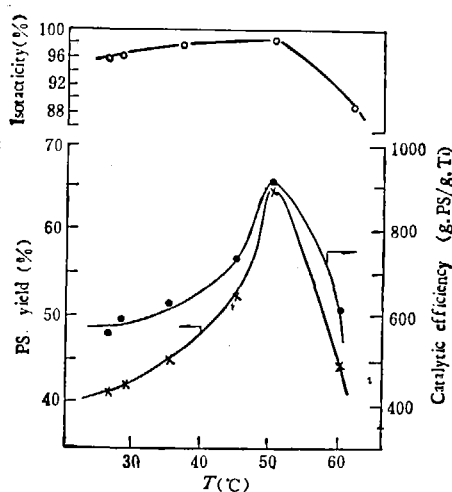


Fig. 4 Correlation of PS yield, isotacticity and catalytic efficiency with polymerization temperature

[Styrene] = 10% (vol); [Ti] = 1.5 mmol/l;
[Al(C₂H₅)₃] = 14 mmol/l; Polym. time: 2 h.

temperature the polymerization rate is slower, while at too high temperature complex reaction would occur, both of these cases will limit the activity of catalyst.

2. Molecular weight of isotactic polystyrene

Monomer concentration: The relation of number average molecular weight, $\bar{M}_n$, of isotactic polystyrene with the starting monomer concentration is shown in Figure 5. The molecular weight increases with the square of monomer concentration. This is another character of SN-1 catalyst for styrene polymerization concerning somewhat special mechanism of chain propagation.

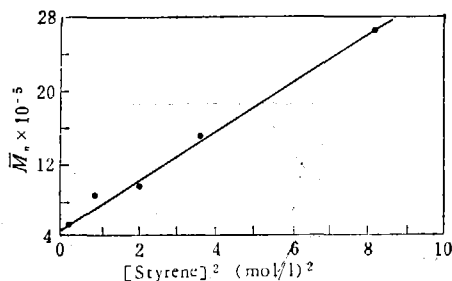


Fig. 5 Linear correlation of i-PS molecular weight with the square of starting styrene concentration

(Polymerization condition: the same as in Fig. 1)

Catalyst concentration and molar ratio of [Al]/[Ti]: The effect of [Al]/[Ti] and [Ti] on the molecular weight of isotactic polystyrene are shown in Figure 6. At the range of [Ti] = 1.5–3 mmol/l or [Al]/[Ti] = 4.3–10 mol/mol, $\bar{M}_n$ values of isotactic polystyrene keep within 7.5–8.5 $\times 10^5$. Meanwhile the yield, catalytic efficiency and the isotacticity are all at very high level as already shown in Figure 2.

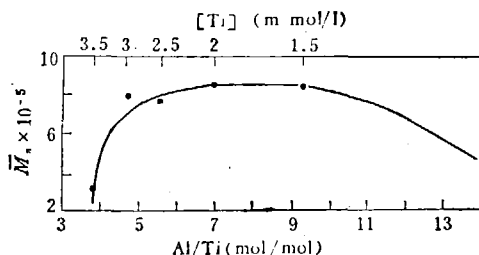


Fig. 6 Correlation of i-PS molecular weight with molar ratio of Al/Ti and [Ti]

(Polymerization condition: the same as in Fig. 3)

Either too high or too low catalytic concentration will cause a depression of molecular weight of isotactic polystyrene from the above value, because in the former case reaction mass will rapidly turn into gummy state retarding polymerization to go farther inversion, while in the latter case polymerization runs too slowly and the chain transfer reaction with triethylaluminum will be relatively more favorable than before.

Polymerization temperature: Figure 7 shows that the molecular weight of isotactic polystyrene increases with temperature in the range of 27–40°C, and keeps almost steadily at 40–50°C with $\bar{M}_n$ values around $8.0\text{--}8.5 \times 10^5$. At lower polymerization temperature, the chain transfer reaction with triethylaluminum will be more favorable than the chain propagation reaction and giving lower molecular weight of polystyrene.

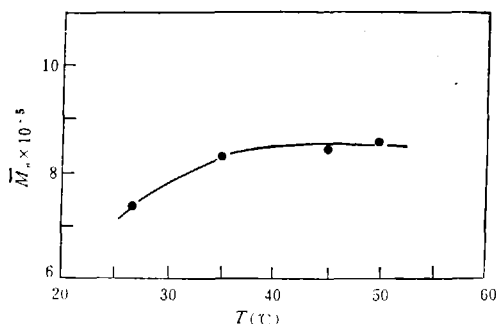


Fig. 7 Correlation of i-PS molecular weight with polymerization temperature (Polymerization condition: the same as in Fig. 4)

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