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Syndiotactic polymerization of styrene in the presence of $CpTiCl_2(OC_6H_4X)$/MAO catalytic systems

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$CpTiCl_2(OC_6H_4X\text{-}p)$ complexes (where $X = CH_3$, Cl, NO_2,; Cp = cyclopentadienyl) activated with methylaluminoxane (MAO) were used in syndiotactic polymerization of styrene. High activity and selectivity for all catalysts were found. The styrene conversion and reaction selectivity depend on the catalyst ageing time and temperature, polymerization temperature and the nature of the substituent in the phenoxy ring. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: polystyrene; syndiotactic polymerization; hemititanocenes; polymerization ageing time

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INTRODUCTION

Our studies of $CpTiCl_2(OC_6H_4X\text{-}p)/BuLi(Et_2AlCl)$ systems, where $X = CH_3$, Cl, NO_2, H, OCH_3, showed that their activity for the hydrogenation and polymerization of olefins depended on electrodonor or electroacceptor properties of the X substituents according to their Hammett factor values. Increase in the reaction rate is proportional to the increasing phenoxy ligand donor properties. The determining factor that increases the catalyst activity is the raised electron density around the titanium ion.[1]

When methylaluminoxane (MAO) is used as an alkylating agent, these catalysts show high activity and selectivity in the syndiotactic polymerization of styrene.[2,3] In this paper, results of styrene polymerization obtained for catalysts with CH_3, NO_2 and Cl phenoxy ligands are presented. The polymerization reactions were carried out with the catalysts aged for various times at 30, 50, 70 and 90 °C.

EXPERIMENTAL

Each operation was performed under an argon atmosphere. The gas was free of water and oxygen.

Benzene, toluene and hexane (POChem — pure) were dried over Na/K alloy. Styrene was distilled from CaH_2 just before polymerization. MAO was purchased from WITCO as a 10% solution in toluene.

$CpTiCl_2(OC_6H_4NO_2-p)$, $CpTiCl_2(OC_6H_4CH_3-p)$ and $CpTiCl_2(OC_6H_4Cl\text{-}p)$ complexes were prepared as described in the literature.[4,5]

The ^1H NMR analyses were performed on samples dissolved in deuterated benzene containing tetramethylsilane (TMS) as internal chemical shift reference, using a Varian 200 instrument. The purity of the complexes synthesized was determined from the position and intensity of the signals corresponding to the cyclopentadienyl ring, the phenoxy ring, and the substituents of the phenoxy ring protons respectively. $CpTiCl_2(OC_6H_4CH_3-p)$, NMR(C_6D_6): δ 6.64–6.53 (4H, m), 5.79 (5H, s), 1.83 (3H, s); $CpTiCl_2(OC_6H_4NO_2-p)$, NMR(C_6D_6): δ 7.52 (4H, d), 6.23 (5H, s); $CpTiCl_2(OC_6H_4Cl\text{-}p)$, NMR($C_6D_6$): δ 6.92 (2H, d), 6.51 (2H, d), 6.01 (5H, s).

Molecular weight measurements were determined using a high-temperature Waters 150-CV gel permeation chromatograph, with 1,2,4-trichlorobenzene as a solvent.

The percentage of syndiotactic fraction (PSF) in the polystyrenes obtained was calculated as the percentage weight of the polymer fraction insoluble in boiling acetone (6 h under reflux).[6]

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Table 1 Yield, syndiotacticity index, average molecular weight and molecular weight distribution of polystyrenes obtained with $CpTiCl_2(OC_6H_4X\text{-}p)$/MAO catalytic systems.

	Ageing time 0 min				Ageing time 15 min				Ageing time 30 min			
T* (°C)	Y (%)	PSF (%)	$10^4 M_w$ (g mol^{-1})	WD	Y (%)	PSF (%)	$10^4 M_w$ (g mol^{-1})	WD	Y (%)	PSF (%)	$10^4 M_w$ (g mol^{-1})	WD
$CpTiCl_2(OC_6H_4CH_3)$												
30	35.8	81.1	122	3.2	26.7	76.1	116	3.0	22.7	75.5	119	2.9
50	41.6	84.3	67	3.8	25.9	76.9	60	5.0	16.3	81.0	61	2.2
70	42.7	79.5	38	3.2	12.6	71.6	31	5.1	11.3	72.5	35	2.1
90	31.0	74.2	37	3.2	8.6	54.8	29	3.7	10.8	49.9	32	3.4
$CpTiCl_2(OC_6H_4NO_2)$												
30	12.3	77.4	57	2.3	19.2	78.7	110	3.3	—	—	—	—
50	38.0	81.0	47	3.4	21.6	79.4	57	4.3	28.1	76.5	33	3.1
70	40.8	76.0	40	2.0	16.3	74.5	27	4.2	15.1	73.7	40	1.8
90	33.2	59.3	33	3.2	16.0	66.5	32	4.1	13.2	48.0	36	2.7
$CpTiCl_2(OC_6H_4Cl)$												
30	22.4	78.4	116	3.1	14.4	73.6	63	2.8	13.9	75.3	78	3.3
50	24.2	70.4	47	3.1	17.8	78.7	50	4.5	14.7	68.8	43	3.5
70	29.8	78.4	32	2.3	12.1	88.8	27	3.7	11.8	71.3	47	4.0
90	28.1	64.0	37	3.4	15.2	58.0	32	4.4	13.6	57.2	34	2.4

Syndiotactic polymerization of styrene was carried out at 30, 50, 70 and 90 °C according to combinatorial catalysis rules[7] in nine Schlenk reactors immersed in a water bath. The reactors were linked to a vacuum–argon line. The sequence of the reactants added to the reactor was as follows: 5 ml MAO solution, the titanium complex solution in toluene (added to the three out of nine reactors), 10 ml of styrene (added 0, 15 and 30 min after the titanium complex addition). The Ti/Al/styrene ratio was 1:300:8000 (0.01 mmol Ti).

Methanol was added to the reactor after 1 h to complete polymerization. A methanol solution of HCl (5%) was added to coagulate the polymer. The final products were separated and dried to constant weight under vacuum at 90 °C.

RESULTS

Combinatorial catalysis, which consists in the use of a series of reactors taken in sufficient number operated under the same conditions, allows us to make tests for variable parameters. This technique minimizes the effect of external agents, and allows us to reject discrepancies. We can also obtain many results in a relatively short time.[7] In this case, application of nine reactors allows for testing three catalysts at the same time:

- at one temperature;
- for different ageing times (i.e. the time the titanium complex reacts with MAO before styrene addition).

By repeating experimental series at constant temperatures we attempted to examine the effect of:

- ageing time and ageing temperature
- reaction temperature
- phenoxy ligand substituent

on the reaction yield Y, product purity as determined by the PSF, average molecular weight M_w and molecular weight distribution (WD) of the polymers obtained. The results are presented in Table 1.

These results indicate that the $CpTiCl_2(OC_6H_4CH_3\text{-}p)$/MAO system is the most active for all temperatures and ageing times investigated. The highest polymer yields (styrene conversion about 42%) are obtained at temperatures 50–70 °C for this catalyst (ageing time is 0 min).

The $CpTiCl_2(OC_6H_4Cl\text{-}p)$/MAO system exhibits yields of 24–28% for 0 min ageing time. In this case, a temperature increase and longer ageing time have no influence on the reaction yield, and an insignificant effect on its growth. For other catalytic systems a higher temperature decreases the reaction yield.

For the temperature range 30–70 °C the PSF in the polystyrenes obtained is higher than 70% for all catalytic systems studied. At 90 °C the PSF has a lower value. A decrease of this value (below 50%) was observed for catalysts with *p*-methylphenoxy and *p*-nitrophenoxy ligands when the ageing time was 30 min.

The highest average molecular weights of syndiotactic polystyrenes were obtained for complexes with *p*-methylphenoxy ligands. Their M_w value is about 120 000 g mol^{-1} for all reactions performed at 30 °C. An increase in the reaction and ageing temperatures results in decreased molecular weights of polymers for all the catalysts (values range 30 000–40 000 g mol^{-1} at temperatures 70–90 °C).

When the ageing time was 0 min, the molecular weight distribution index was about 3. This index increased to a value of 4–5 for an ageing time of 15 min. When the ageing time was 30 min the polystyrenes obtained showed this index to have been lowered again (WD values below or near 3).

DISCUSSION AND CONCLUSIONS

Substituents at phenoxy ligands have different electrodonor–acceptor properties as described by the Hammett factor σ_p of 0.78, 0.23, −0.17 for NO_2, Cl, CH_3 respectively.[8]

These properties have no influence on selectivity (PSF value) of the catalysts investigated. The temperature is a controlling factor here. Selectivity was approximately the same for all the catalysts when the reactions were performed at from 30 to 70 °C. Reactions at 90 °C showed a lower selectivity.

Studies on the catalyst working mechanism suggest the titanium(III) ion to be the active form bonded only to the cyclopentadienyl ring. There is no other initial ligand at this stage, and their places are occupied by the coordinated styrene monomer, the growing polymer chain and the phenyl ring of the last monomer in the polymer chain.[9,10] For this reason, all the monocyclopentadienyl titanium catalysts for syndiotactic polymerization of styrene should exhibit the same selectivity. The formation of other isomers can be a result of the presence of other catalytic forms. The results obtained show similar working mechanisms for all the catalysts and indicate some unselective catalytic forms to be involved at temperatures higher than 70 °C.

The reaction temperature, rather than the phenoxy ring ligands, has a controlling effect on the molecular weights of the polystyrenes obtained. Only the reaction performed below 30 °C gives a polymer with an average molecular weight over 100 000. A temperature increased to 70–90 °C decreases the average molecular weight, which is approximately the same for all the catalysts. The model for the active catalyst form mentioned above explains these relationships. A higher temperature makes detaching of the polymer chain from the titanium catalytic centre easier.

On these grounds, we can expect that a cyclopentadienyl ring only affects the styrene polymerization yield. But for catalysts with additional structural features containing the cyclopentadienyl ring, initial substituents (not existing in active catalyst forms) have a large effect on their activity. This effect is different and depends on electrodonor–acceptor and steric factors characteristic of a given ligand. Previous studies on $CpTiX_3$/MAO systems in styrene polymerizations indicate that an increase in activity can be achieved by the replacement of chloro by (more electroacceptor) fluoro ligands.[11] When X is an alkoxy group in $CpTiX_3$/MAO systems, the alkyl ligand donor effect is an activating factor in butadiene polymerization.[12] The steric properties of the ligand also affect the catalyst activity.[13]

This effect is related to the yield of an active catalyst form described by the reactions in Eqns [1]–[3]:

$$CpTiX_3 + MAO(Me) \leftrightarrow CpTiMe_3 + MAO(X) \quad (1)$$

$$CpTiMe_3 \leftrightarrow CpTiMe_2 + Me \quad (2)$$

$$CpTiMe_2 + MAO(X) \leftrightarrow CpTiMe^+ + [(Me)MAO(X)]^- \quad (3)$$

In reaction [1] $CpTiX_3$ is alkylated to $CpTiMe_3$, which in the second step undergoes a homolytic reductive dissociation to $CpTiMe_2$. In this next step titanium(IV) is reduced to titanium(III) (this can also be accelerated by new MAO(X)). The new MAO(X) form, with X ligands, playing the role of a Lewis acid, detaches methyl anions from $CpTiMe_2$ to give the cationic catalyst active form. This form complexes styrene, which subsequently is inserted into the Ti—Me bond.[9,12,14]

This mechanism shows that X ligands affect $CpTiX_3$ alkylation yield, MAO(X) acceptor proper-

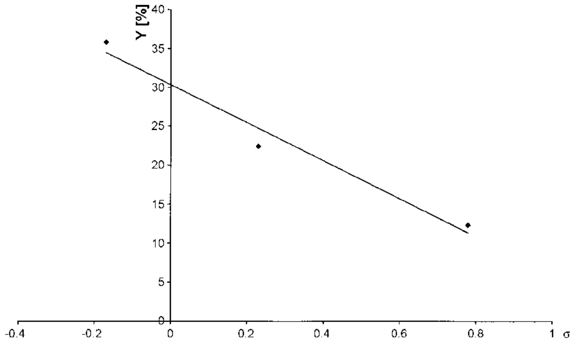

Figure 1 Yield of styrene polymerization at 30 °C with $CpTiCl_2(OC_6H_4X\text{-}p)$/MAO catalytic systems, as a function of substituent Hammett factors.

ties, and in various ways also affect reactions [1]–[3].

Our results indicate the lowest activity for the NO_2-substituent catalyst and the highest activity for the catalyst with a CH_3 group when the reaction is performed at 30 °C. Phenoxy rings in the former catalyst have the same effect on styrene polymerization as alkoxy groups in butadiene polymerization mentioned before. At 50 and 70 °C the reaction yields were approximately the same for these two catalysts (and relatively higher from reaction yields obtained for the $CpTiCl_2(OC_6H_4Cl\text{-}p)$ catalyst). At 90 °C the catalysts with CH_3 and NO_2 substituents decreased the activity, whereas the catalyst with a Cl ligand did not show such an effect.

Activity of the catalysts at 30 °C correlates with the Hammet factors of the phenoxy ligand substituents (Fig. 1).

This correlation shows that the electrodonor influence of the substituents increases catalyst activity at 30 °C. At higher temperatures there is no such correlation observed. The results obtained suggest that the $—OC_6H_4NO_2$ ligand is more electrodonating than is the $—OC_6H_4Cl$ ligand. We observed that nitroaromatic compounds react with Me_3Al of MAO to produce alkylocyclohexadiene anions with a negative charge probably localized on the nitro group. A similar reaction occurs when Grignard reagents are made to react with nitro aromatic compounds.[15] In our case, a similar reaction probably occurred at temperatures higher than 30 °C.

The results obtained from the study of syndiotactic styrene polymerization show that all factors studied, *viz.* ageing time, reaction temperature and phenoxy ring ligands, have an effect on the reaction yield. The best yields are obtained when styrene is added to the reaction mixture immediately after MAO addition. For ageing times of 15 and 30 min the yields are similar. We presume that the catalyst studied undergoes a rapid deactivation without contact with styrene. Deactivation is faster at higher temperatures. This effect is the lowest for a catalyst with chlorophenoxy substituents.

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