Note

[Cp$_2$TiCl$_2$] as polymerization catalyst in aqueous medium: polymerization of styrene in water

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Abstract

The contrary to the general idea, an early transition metal organometallic compound, [Cp$_2$TiCl$_2$] has been found to be active catalyst for aqueous medium polymerization of styrene.
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1. Introduction

Aqueous catalytic polymerization seems like a contradiction at first sight, because of the high moisture sensitivity of the Ziegler–Natta catalysts. However, there is a strong commercial and environmental driving force to develop an aqueous route to polyolefin having desired property [1]. Free radical initiated emulsion polymerization of olefins is well known. A large numbers of reports have appeared on the catalytic systems capable of polymerization in aqueous medium involving mainly late transition metal catalysts [2–4]. A recent report deals with syndiospecific polymerization of styrene in water–toluene biphasic medium using [(C$_5$Me$_5$)Ti(OMe)$_3$] catalyst along with a borate and an alkylaluminium compound as activators and cationic or neutral surfactant as emulsifier [5]. Development of an early transition metal based catalyst system for polymerization of olefin in aqueous medium without using any organic solvent or any activator such as MAO or other alkyl aluminum compounds or borate still remains a challange.

Herein, we present first report on polymerization of styrene in aqueous medium catalyzed by [Cp$_2$TiCl$_2$] without using any co-catalyst.

2. Experimental

All the polymerization reactions were carried out under argon atmosphere in degassed water. The polymerization reactions were also carried out in the presence of air as well as in the presence of radical scavengers. It may be noted that, no major difference was observed in the results obtained under both the reaction conditions. Commercial styrene was purified by usual method. Commercially obtained SDS was used without purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200, 200 MHz NMR spectrometer in CDCl$_3$ solutions at room temperature. IR spectra were recorded on a Perkin–Elmer Model 883 spectrometer. The thermal measurements and differential scanning calorimetry (DSC) were done on a Shimadzu DT 40 thermal analyzer. The heating rate was 10 °C/min. Powder XRD were done on a Philips XRD model 1729 powder diffractometer. Molecular weights were measured by GPC using Merck Hitachi L 7100 LaChrom instrument using PL gel 5μ, mixed C column in chloroform solution. The flow rate was 1 mL/ min. The standard used was polystyrene.

2.1. Polymerization of styrene

Cp$_2$TiCl$_2$ (0.1245 g; 0.0005 mol) was suspended in water (20 mL) and this suspension was stirred for about 1 h, whereupon a yellow solution was obtained. Sodium

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n-dodecyl sulfate (SDS)/Cetyltrimethyl ammonium bromide (CTAB) (1.6×10^{-3} mol) was dissolved in water (80 mL). To this was added styrene (5.2 g; 0.05 mol) and the whole were stirred for 1 h. To the emulsified monomer solution was then added the aqueous solution of Cp_2TiCl_2. The polymerization mixture was then placed in an oil bath maintained at the desired temperature and the reaction mixture was stirred for required time period. The reaction was quenched by the addition of the emulsion to a mixture of methanol (200 mL) and hydrochloric acid (20 mL). The precipitated polystyrene was then filtered, washed repeatedly with water and methanol and dried in vacuo at ambient temperature. The polymer was extracted with refluxing acetone for 3 h to remove low molecular weight fraction of the polymer. The polystyrene was purified by dissolving it in toluene and precipitation by the addition of methanol and dried in vacuo.

3. Results and discussion

Polymerization reactions were carried out in a temperature range 10–90 °C under argon atmosphere. It may be mentioned that, similar results were obtained when the reactions were carried out in the presence of air. Polymerization was initiated by the addition of an aqueous solution of Cp_2TiCl_2 (0.0005 mol in 20 mL water) to the emulsified (1.6×10^{-3} mol of SDS in 80 mL of water) styrene (0.05 mol). The polymerization mixture was then placed in an oil bath maintained at the desired temperature and the reaction mixture was stirred for required time period. The reaction was quenched by the addition of the emulsion to a mixture of methanol and hydrochloric acid.

Details of the preliminary results of polymerization using Cp_2TiCl_2 in water in the presence of anionic surfactant, SDS are given in Tables 1 and 2.

The average molecular weights, measured by GPC (against standard polystyrene) lies in the range 690,000–540,000 and is found to be much higher than the ordinary commercially available polystyrene [6]. On an average M_w/M_n ratio is found to be 1.7, which is fairly narrow and indicative of a single site catalyst [7]. Also,

the elemental analyses (C&H) of the polymer agree very well with that of styrene.

The differential scanning calorimetry of the polymer shows glass transition temperature (T_g) at ca. 100 °C, typical of atactic polystyrene, and an endotherm at 423 °C due to de-polymerization [8]. The TGA as well as DTA experiments clearly show that, the decomposition takes place in a single step as observed earlier [8].

The ^{13}C and ^1H NMR spectra of the newly synthesized polymer and those of atactic polystyrene, synthesized by radical polymerization, are similar. The powder X-ray diffraction pattern of the polymer in the pellet form does not show any crystallinity, as expected. The FT-IR spectra of the polymer show typical bands due to polystyrene [9]. Thus, X-ray diffraction, thermal studies, ^{13}C and ^1H NMR and FT-IR evidences confirm the atactic nature of the polystyrene obtained.

It has already been shown that, in the homogeneous Ziegler–Natta catalyst, $[Cp_2TiMe]^+$ is responsible for stereospecific polymerization [10]. It is also well known that, Cp_2TiCl_2 when dissolved in water, gives $[Cp_2Ti(OH)]^+$ in solution as one of the major products [11]. Our general synthetic approach is in situ formation of $[Cp_2Ti(OH)]^+$ form aqueous solution of Cp_2TiCl_2 and stabilisation of this cation by large, soft and non-coordinating anion, *n*-dodecyl sulfate, and utilization of $[Cp_2Ti(OH)]^+$ as polymerization catalyst. Polymerization by Cp_2TiCl_2 in aqueous medium without using any surfactants failed. Also, polymerization using cationic surfactant, cetyltrimethylammonium bromide (CTAB) was unsuccessful, thus providing evidence that, stabilisation of $[Cp_2Ti(OH)]^+$ is important in showing catalytic activity. As the hydroxyl group of $[Cp_2Ti(OH)]^+$ is labile, the end group of the polymer in this case, is expected to be –OH group. The ^1H NMR of the polymer shows a weak signal at 4.1 ppm due to the –CH proton linked to the end group –OH.

The molecular weight and M_w/M_n data clearly show that the efficiency of the catalyst is only few percent and also with the increasing polymerization temperature, the molecular weight increases and yield decreases. It has already been shown that, an aqueous solution of Cp_2TiCl_2 when refluxed for several hours affords undecomposed Cp_2TiCl_2 along with TiO_2 [12,13]. Also, it

Table 1
Polymerization of styrene with Cp_2TiCl_2 at different temperature using different surfactant[a]

Cp_2TiCl_2 (mol)	Styrene (mol)	Surfactant ($\times 10^{-3}$ mol)	T (°C)	M_w	M_w/M_n	Yield (%)	T_g (°C)
0.0005	0.05	SDS (1.6)	30	–		–	–
0.0005	0.05	SDS (1.6)	50	540 000	1.8	73.1	110
0.0005	0.05	SDS (1.6)	70	688 000	1.7	46.2	100
0.0005	0.05	SDS (1.6)	90	690 000	1.7	5.8	115
0.0005	0.05	CTAB (1.6)	50	–		–	–
0.0005	0.05	CTAB (1.6)	70	–		–	–
0.0005	0.05	–	50	–		–	–

[a] Reaction time: 6 h, T: polymerization temperature, M_w: molecular weight (GPC), T_g: glass transition temperature (DSC), yield: acetone insoluble fraction, styrene concentration: 0.5 mol/L.

Table 2
Polymerization of styrene using different concentration of SDS and Cp$_2$TiCl$_2$[a]

Cp$_2$TiCl$_2$ (mol)	Styrene (mol)	SDS ($\times 10^{-3}$ mol)	M_w	M_w/M_n	Yield (%)
0.0005	0.05	SDS (0.8)	[b]	[b]	6.3
0.0005	0.05	SDS (1.6)	540 000	1.8	73.1
0.0005	0.05	SDS (2.4)	550 000	1.7	78.2
–	0.05	SDS (1.6)	–	–	–
0.00025	0.05	SDS (1.6)	[b]	[b]	[c]
0.00075	0.05	SDS (1.6)	[b]	[b]	40.4

[a] Reaction condition – polymerization time: 6 h, polymerization temperature: 50 °C, M_w: molecular weight (GPC), yield: acetone insoluble fraction, styrene concentration: 0.5 mol/L.
[b] Not determined.
[c] Very small amount.

is known that, at room temperature Cp$_2$TiCl$_2$ under goes hydrolysis and gives polytitanoxanes along with [Cp$_2$Ti(OH)]$^+$ [14]. Since the TiO$_2$ and other hydrolysis products are catalytically inactive, the efficiency of the catalyst is found to be less than expected. Since at higher temperature, the extent of decomposition of the catalyst is higher, the conversion decreases at higher polymerization temperature.

We have carried out polymerization using different catalyst and SDS concentration (Table 2). It has been observed that a minimum of one mole percent of the catalyst is required for polymerization. The result shows that, conversion decreases with the increase in catalyst concentration. It may be noted that, a similar observation was made Mani and Burns [15] earlier. Attempted polymerization using critical miceller concentration [CMC] (0.8 × 10^{-3} mol) of SDS afforded very low yield of the polymer. However, using double or triple of the CMC significant yield of the polymer can be obtained and beyond this we could not observe any significant effect of the SDS concentration on the polymerization.

Albeit, a large number of Ziegler–Natta catalytic systems afford atactic polystyrene as well as polypropylene [16–18], the atactic nature of the polymer obtained by the present catalytic system initially led us to believe that, in the present case a free radical polymerization or spontaneous polymerization [19–21] may be in operation. Attempted polymerization without the addition of Cp$_2$TiCl$_2$, failed. This clearly shows that, Cp$_2$TiCl$_2$ catalyzes the polymerization reactions and the polymerization is not a spontaneous polymerization. Dioxygen is a strong inhibitor for radical polymerization of styrene [22] and is known to increase the in-

duction time and decrease the molecular weight of the polymer [20]. We have carried out polymerization reactions in the presence of dioxygen and we could neither observe any increase in the induction period, nor could we observe any major difference in the molecular weight of the polystyrene (Table 3). The fact that, Cp$_2$TiCl$_2$ undergoes photo-dissociation to generate Cp$^\cdot$ and CpTi(III)Cl$_2^\cdot$ prompted us to carry out polymerization in the absence of light. No difference was observed between the polymerization reaction carried out in the presence or absence of light (Table 3). Also, we have carried out polymerization reaction using styrene without removing stabilizer (4-*tert*-butylcatechol) (Table 3).

In this case, we could not see any inhibitory affect of the stabilizer. These observations clearly rule out free radical polymerization. However, addition of potassium fluoride and chloride (Ti:F$^-$/Cl$^-$ ratio was maintained at 1:2) completely inhibits polymerization. Similarly, AlCl$_3$ was found to inhibit polymerization. This may be explained by the fact that, fluoride or chloride ions occupy the vacant coordination sites and destroy the cation, [Cp$_2$Ti(OH)]$^+$, and thus inhibit polymerization. We have also generated, in situ, the cations [Cp$_2$Ti(acac)]$^+$ (acacH = acetylacetone) [11] and [(H$_2$O)Cp$_2$Ti(μ-O)Ti(H$_2$O)Cp$_2$]$^{2+}$ [23] by reaction of Cp$_2$TiCl$_2$ with acetylacetone and Na$_2$S$_2$O$_6 \cdot$2H$_2$O, respectively, in water and used these cations successfully for polymerization. In order to further establish the mode of action of the catalyst, we have carried out polymerization using [Cp$_2$ZrCl$_2$] as an initiator. Unlike titanium, radical formation is not expected in this case. The initial results show that, [Cp$_2$ZrCl$_2$] is equally effective as a catalyst for the polymerization of styrene in water. Work on the

Table 3
Polymerization of styrene with Cp$_2$TiCl$_2$ using SDS under various experimental conditions[a]

Reaction atmosphere	Light/dark	Stabilizer (4-*tert*-butylcatechol)	M_w	M_w/M_n	Yield (%)
Argon	Light	Absent	540 000	1.8	73.1
Argon	Light	Present	[b]	[b]	70.0
Argon	Dark	Absent	[b]	[b]	68.0
Air	Light	Present	535 000	1.7	69.5

[a] Reaction condition – polymerization time: 6 h, polymerization temperature: 50 °C, M_w: molecular weight (GPC), yield: acetone insoluble fraction, styrene concentration: 0.5 mol/L, [Ti]: 0.005 mol/L.
[b] Not determined.

zirconium compound is in progress. It is well known that, methylmethacrylate is not sensitive to cationic polymerization. Attempted polymerization of methylmethacrylate by the present catalytic system was successful [24]. Acrylonitrile is known to undergo polymerization by radical and anionic initiators. We have attempted polymerization of acrylonitrile by this system and could not obtain any polymer. Thus, this observation rules out anionic mechanism. All these experimental facts point towards a coordination polymerization mechanism. The inhibitory effect of fluoride and chloride and the successful use of the other water-soluble cations as well as [Cp$_2$ZrCl$_2$] as catalysts clearly indicate that, a coordination polymerization is operative in this case.

Water as a solvent has attracted a lot of attention in recent times [1,2]. This trend can be related to the fact that, it is a comparatively environmentally benign solvent and its inflammability as well as high heat capacity is highly advantageous. A simple method has been developed to demonstrate how the oxophilicity of early transition metal compounds can be advantageously used for generating an active catalyst for polymerization.

4. Conclusion

In conclusion, a simple method has been developed to demonstrate how the oxophilicity of an early transition metal compound can be advantageously used for generating an active catalyst for polymerization.

Acknowledgements

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