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[Cp_2TiCl_2] Catalyzed polymerization in water: polymerization of methylmethacrylate to a high molecular weight polymer

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Abstract

An early transition metal metallocene compound, Cp_2TiCl_2, has been used as a catalyst in aqueous emulsion polymerization of methylmethacrylate to high molecular weight polymer with an anionic surfactant, sodium *n*-dodecyl sulfate (SDS) as emulsifier. The added surfactant has been found to play the dual role of stabilizer of the cation as well as an emulsifying agent for the monomer. Reactions with cationic (cetyltrimethylammonium bromide) emulsifiers were not successful under the conditions examined.

Keywords: Aqueous medium; Polymethylmethacrylate; Titanocene dichloride

1. Introduction

Polymerizations carried out in aqueous media are receiving more and more attention and in contrast to the numerous controlled polymerization methods employed in organic media, aqueous polymerization is mainly focused on radical polymerization. Among the most important factors contributing to this trend are increased environmental concern and a sharp growth of pharmaceutical and medical applications for hydrophilic polymers [1]. A large numbers of reports have appeared on the development of catalytic systems capable of polymerization in aqueous medium, these involve mainly late transition metal catalysts [2–5]. A recent report deals with syndiospecific polymerization of styrene in water–toluene biphasic medium using [$(C_5Me_5)Ti(OMe)_3$] catalyst along with a borate and an alkylaluminium compound as activators and a cationic or neutral surfactant as emulsifier [6]. However, the use of early transition metal catalysts like those of titanium and zirconium metallocene compounds as polymerization catalysts in aqueous medium still remains a challenge. We were interested in developing 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 aluminium compounds or borate. Recently, we have reported aqueous emulsion polymerization of styrene with Cp_2TiCl_2 [7].

Herein we present first report on polymerization of methylmethacrylate (MMA) in aqueous medium catalyzed by titanocene dichloride without using any co-catalyst.

2. Experimental section

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 methylmethacrylate was purified by usual method. Commercially obtained SDS was used without purification. ^1H 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 (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

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column in chloroform solution. The flaw rate was 1 ml/min. The standard used was polystyrene.

2.1. Polymerization of methylmethacrylate (MMA)

Cp_2TiCl_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 *n*-dodecyl sulfate (SDS)/cetyltrimethyl ammonium bromide (CTAB) (1.6×10^{-3} mol) was dissolved in water (80 ml). To this was added MMA (5.01 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. In the cases of $[Cp_2Ti(acac)]^+$ (acacH = acetylacetone) and $[(H_2O)Cp_2Ti(\mu\text{-}O)Ti(H_2O)Cp_2]^{2+}$ catalyzed polymerization, the cations were generated by the addition of acetylacetone (0.0005 mol) and $Na_2S_2O_6{\cdot}2H_2O$ (0.0005 mol), respectively, to the aqueous solution of Cp_2TiCl_2 and the reaction solution was stirred for further 30 min prior to the addition to the emulsified MMA. The reaction was quenched by the addition of the emulsion to a mixture of methanol (200 ml) and hydrochloric acid (20 ml). The precipitated polymethylmethacrylate (PMMA) was then filtered, washed repeatedly with methanol and dried in vacuo at ambient temperature. Finally, the polymer was extracted with refluxing acetone for 3 h and filtered to remove any insoluble material and PMMA was precipitated with the addition of excess methanol and dried in vacuo.

3. Results and discussion

Polymerization reactions were carried out in a temperature range 10–90 °C and in a 250 ml round bottomed flask under argon atmosphere. Polymerization reactions were carried out by the addition of an aqueous solution of Cp_2TiCl_2 to emulsified methylmethacrylate (MMA), emulsified by sodium *n*-dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB), and heating the reaction mixture at desired temperature. The reactions were monitored hourly by quenching the reaction by the addition of the emulsion to a mixture of methanol and hydrochloric acid. PMMA obtained was purified by dissolution in acetone and re-precipitation by the addition of methanol.

Details of the preliminary results of polymerization using Cp_2TiCl_2 in water in the presence of anionic surfactant, sodium *n*-dodecyl sulfate (SDS) are given in Table 1.

It has been found that, the conversion is temperature dependent, and up to 40 °C we could not detect any product. The conversion is negligible at 50 °C. The highest conversion was observed at 70 °C, and the conversion drops dramatically at the temperature 90 °C.

The conversion is also found to be dependent on polymerization time. Up to 9 h of reaction time we could observe only little polymerization. After 9 h of reaction time the yield increases steadily rises to a maximum at the reaction time of 11 h.

The average molecular weights, measured by GPC is high and lies in the range 739,000–514,000. The M_w/M_n ratio is found to be 1.6 and clearly shows moderately low molecular weight distribution and indicates a single site catalytic system [8]. Recently, Arnold et al. has reported synthesis of a very high molecular weight (1.41×10^6) isotactic PMMA [8]. This is the highest molecular weight so far reported. The differential scanning calorimetry (DSC) of the polymer shows an endothermic peak at 380 °C due to depolymerization.

The ^1H NMR (200 MHz) spectra at room temperature in $CDCl_3$ shows α methyl peaks at 0.84, 1.01, and 1.25 ppm. These can be assigned to triads [rr], [mr], and [mm], respectively. The $-OCH_3$ protons appear at 3.60 ppm [9]. The relative ratio of the [rr], [mr], [mm] is found to be 60:38:2. The ^{13}C NMR spectra recorded in $CDCl_3$ shows corresponding ^{13}C peaks at 16.6, 18.8, and 19.0 ppm due to α CH_3. The quaternary carbon appears at 44.6, and 44.9 ppm. The $-OCH_3$ carbon appears at 51.7 ppm and the CH_2 carbon appears at 54 ppm. The $-C{=}O$ carbon appears at 176.9, 177.1, 177.8, and 178.0 ppm. These peaks can be assigned to [mmmm], [mmrr + rmmr], [rrrr], and [rrrm] of the pentad distributions [10]. We could not observe the weak signals of [mmmr] and [mrrm] conformations. The IR spectra of the polymer show typical bands due to PMMA [11]. No bands could be observed in the region 3600–3300 cm^{-1}, thus clearly showing that, no hydrolysis of the ester group, during the reaction, has taken place.

The powder X-ray diffraction pattern of the polymer in the powder form shows a broad peak at $2\theta = 29.3$ and 13.1°.

It has already been shown that, in the homogeneous insertion catalysis, coordinatively unsaturated and electron deficient species are active catalysts for polymerization [2–5]. 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 [12]. Our general synthetic approach is in situ formation of coordinatively unsaturated and electron deficient species, $[Cp_2Ti(OH)]^+$, from aqueous solution of Cp_2TiCl_2 and stabilization of the cation by a large, soft, and weakly coordinating surfactant anion and utilization of $[Cp_2Ti(OH)]^+$ as polymerization catalyst. The added surfactant is expected to have the dual role of stabilizer of the cation as well as an emulsifying agent for the monomer. Attempted 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, stabilization 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, in all probability, is $-OH$ group.

Cp_2TiCl_2 is known to undergo photo-dissociation to

Table 1
Polymerization of MMA with Cp_2TiCl_2 at different temperature using different surfactant

Catalyst (mol)	MMA (mol)	Surfactant ($\times 10^{-3}$ mol)	T (°C)	M_w	Yield (g) (%)
Cp_2TiCl_2 (0.0005)	0.05	SDS (1.6)	30	–	–
Cp_2TiCl_2 (0.0005)	0.05	SDS (1.6)	50	–	–
Cp_2TiCl_2 (0.0005)	0.05	SDS (1.6)	70	514,000	3.5 (70.0)
Cp_2TiCl_2 (0.0005)	0.05	SDS (1.6)	90	739,000	1.00 (20.0)
Cp_2TiCl_2 (0.0005)	0.05	CTAB (1.6)	50	–	–
Cp_2TiCl_2 (0.0005)	0.05	CTAB (1.6)	70	–	–
Cp_2TiCl_2 (0.0005)	0.05	–	70	–	–
$[Cp_2Ti(acac)]^+$ (0.0005)	0.05	SDS (1.6)	70	[a]	2.1 (42.0)
$[\{(H_2O)Cp_2Ti\}_2(\mu\text{-}O)]^{2+}$ (0.0005)	0.05	SDS (1.6)	70	[a]	1.9 (38.0)

Reaction time, 11 h. T, polymerization temperature, M_w, molecular weight (GPC), MMA concentration, 0.5 mol/l [Ti] = 0.005 mol/l.

[a] Not determined.

generate Cp· and $CpTi(III)Cl_2$· and the observed triad distribution, which is similar to the typical stereostructure of free radical PMMA led us to believe that, in the present case a free radical polymerization may be in operation. Polymerization reactions have been carried out in the absence of light. We could not observe any difference between the polymerization reaction carried out in the presence and that in the absence of light. Similarly, attempted polymerization without the addition of Cp_2TiCl_2, both in argon atmosphere and under ambient condition, failed. Dioxygen is a known strong inhibitor for the free radical polymerization [13,14]. Dioxygen usually increases induction time and reduces molecular weight of the polymer obtained [13,14]. We have carried out polymerization reactions in the presence of dioxygen and could neither observe any increase in the induction time, nor could we observe any major difference in the molecular weight of the PMMA obtained. We have also carried out the polymerization of MMA without removing stabilizer (hydroquinone) from MMA and PMMA of similar molecular weight was obtained form these reactions. These results clearly show that, Cp_2TiCl_2 catalyzes the polymerization reactions and the polymerization is neither a spontaneous thermal polymerization, nor a radical polymerization. However, addition of potassium fluoride or chloride ($Ti:F^-/Cl^-$ ratio was maintained at 1:2) completely inhibits polymerization. Similarly, addition of $AlCl_3$ ($Ti:AlCl_3 :: 1:1$) inhibits polymerization. This may be explained by the fact that, fluoride/chloride ions occupy the vacant coordination sites and destroy the cation and thus inhibit polymerization. We have also generated, in situ, the cations $[Cp_2Ti(acac)]^+$ (acacH = acetylacetone) [12] and $[(H_2O)Cp_2Ti(\mu\text{-}O)Ti(H_2O)Cp_2]^{2+}$ [15] by reaction of Cp_2TiCl_2 with acetylacetone and $Na_2S_2O_6 \cdot 2H_2O$, respectively, in water and used these cations successfully for polymerization. Unlike in the case of $[Cp_2TiCl_2]$, radical formation is not very facile in the case of $[Cp_2ZrCl_2]$. The initial results show that $[Cp_2ZrCl_2]$ is equally effective as a catalyst for the polymerization of MMA in water. Work on the zirconium compound is in progress. The inhibitory effect of fluoride and chloride and the successful use of the other water-soluble cations and $[Cp_2ZrCl_2]$ as catalysts clearly indicate that, a coordination polymerization is operative in this case.

Lower oxophilicity and resistance to hydrolysis have led to the use of late transition metal catalysts for polymerization of polar monomers and aqueous emulsion polymerization. Because of the ease of β-hydride elimination, which typically competes with chain growth, these complexes afford only low molecular weight polymer in aqueous medium [1–5] and generally exhibit reduced activities for olefin insertion relative to early transition metal catalysts [16]. Only few catalysts are known to give high molecular weight products [5]. In contrast, the result presented here shows that, in an aqueous emulsion polymerization, using an early transition metal catalyst, it is possible to obtain high molecular weight polymer containing polar functional groups. As opposed to the late transition metal catalysts, due to the hydrolytic instability of Cp_2TiCl_2 the efficiency of the catalyst is only few percent as indicated by molecular weight and M_w/M_n data. Also, in the present case, with the increasing polymerization temperature, the molecular weight increases and yields decreases. This is due to the hydrolysis of Cp_2TiCl_2 to catalytically inactive polytitanoxanes, and TiO_2 [17] along with active species $[Cp_2Ti(OH)]^+$. Also, at higher temperature, the extent of decomposition of the catalyst is higher, and thus, conversion decreases at higher polymerization temperature.

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.

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