



Aqueous emulsion polymerization of styrene and substituted styrenes using titanocene compounds

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ABSTRACT

Aqueous emulsion polymerization of styrene in the presence of half-titanocenes which CpTiCl_3 , $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$, and of the titanocene $(\text{Ph})_2\text{C}[(\text{Cp})(\text{Flu})\text{Ti}]\text{Cl}_2$ is effected. The polymer features are compared with those of polystyrene obtained in the same reaction conditions, by using Cp_2TiCl_2 as initiator.

Titanocene $(\text{Ph})_2\text{C}[(\text{Cp})(\text{Flu})\text{Ti}]\text{Cl}_2$ does not show any activity in styrene polymerization. On the contrary, by using both half-titanocenes CpTiCl_3 and $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$, stereoirregular polystyrene is produced. Aqueous emulsion polymerization of substituted styrenes (3-methyl-styrene, 4-methyl-styrene, 3-chloro-styrene, 4-chloro-styrene) is also performed in the presence of Cp_2TiCl_2 . From all monomers, stereoirregular polymers are obtained. Monomer reactivity results dependent on the substituent on the aromatic ring. Aqueous emulsion styrene – 4-chloro-styrene copolymerizations are performed by using Cp_2TiCl_2 , too. Copolymer composition totally reflects that of comonomers used in the feeding. According to a statistical distribution of comonomers, the product of the reactivity ratios is 1.1.

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1. Introduction

Aqueous emulsion polymerization is one of the most important industrial polymerization processes [1]. Respect to the most commonly used organic solvent-based systems, water as polymerization medium, exhibits unique properties such as high heat capability and high polarity. Moreover, water is nonflammable and nontoxic, assuring a remarkable economic saving and important attention to the environmental safeguard [1–4].

Since the forties, aqueous emulsion polymerization has been used for the production of polymers replacing natural rubber and, it is today, employed for the polymerization of a variety of monomers like styrene, butadiene, methylmetacrylate, vinyl acetate etc.

In this framework, it is worth recalling that aqueous polymerization has been mainly focused on radical polymerization and, in particular, in recent years, greater attention has been also aimed to the development of transition metal catalyzed aqueous emulsion polymerization techniques. In this regard, due to their low oxophilicity, late transition metal based species like neutral nickel compounds, or cationic palladium complexes have been already tested in aqueous emulsion olefin polymerization [5–10], e.g.,

ethene was polymerized in water by using rhodium species [11]. Stereospecific 1,3-butadiene polymerization in aqueous medium catalyzed by rhodium salts [12,13] or cobalt(I) allyl complexes [14–21] has been also reported.

Due to their high sensitivity to moisture, early transition metal based little investigated in the field of aqueous emulsion olefin polymerization. Their applications were mainly focused in the field of Ziegler-Natta coordination polymerization [22–27]. In the last recent years, the peculiar ability of titanium complexes, like $\text{Cp}_2\text{Ti}(\text{III})\text{Cl}$, that can be easily obtained by reduction with Zn of inexpensive titanium compounds like Cp_2TiCl_2 , to catalyze styrene living radical polymerization initiated by epoxides, peroxides, or aldehydes, was also recognized [28–31]. In fact, organo titanium (III) species catalyze, for example, single electron transfer reduction of aldehydes or radical ring opening of epoxides, leading to formation of radical initiators for styrene living radical polymerization [28–31].

In literature, a few articles by Bhattacharjee et al. dealing with Cp_2MCl_2 (with $\text{M} = \text{Ti}$ or Zr) used as active catalytic precursor for aqueous emulsion polymerization of styrene and methylmethacrylate have been also reported [32–36]. In these papers, the authors hypothesize that the active catalytic specie could be a cation as $[\text{Cp}_2\text{MOH}]^+$, that is one of the species formed by hydrolysis of Cp_2MCl_2 , stabilized by large non-coordinating anion *n*-dodecylsulfate, utilized as emulsified [32–36]. They also propose that

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the polymerization reaction can follow a coordination – insertion mechanism starting from insertion of first monomer unit in the “labile” metal-hydroxyl group bond and, exclude the possibility of free radical or spontaneous polymerization. However, no clear experimental evidence to support this hypothesis has been really reported. Studies on group 4 metallocene compound capability to catalyze aqueous emulsion polymerization involving a coordination mechanism need of further investigation.

Herein, we report on polymerization of styrene in aqueous medium effected using different titanium compounds. Styrene polymerization activities of titanocenes which differ in the ancillary ligands are compared. Experimental studies aimed to clarify the involved polymerization mechanism are also shown.

Moreover, substituted styrenes, like methyl-styrenes and chloro-styrenes, have been also tested in aqueous emulsion polymerization by using Cp_2TiCl_2 . Their polymerization reactivities are compared with that of styrene. Styrene – 4-chloro-styrenes copolymerization results effected by using different ratios of two comonomers are also reported.

2. Experimental section

2.1. General procedure

Styrene and substituted styrenes were purchased by Sigma–Aldrich and, purified by distillation over calcium hydride (CaH_2). Sodium *n*-dodecyl sulphate (SDS), Cp_2TiCl_2 , and CpTiCl_3 (where: Cp = cyclopentadienyl) were purchased by Sigma–Aldrich and used without further purification. $(\text{Ph})_2\text{C}[(\text{Cp})(\text{Flu})\text{Ti}]\text{Cl}_2$ (where: Cp = cyclopentadienyl, Flu = fluorenyl) were purchased by Boulder Scientific and also used without further purification.

$(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$ were synthesized in our laboratories according to the literature [37].

2.2. Polymerization

Polymerization reactions were performed at 50 °C under nitrogen atmosphere, following this general procedure: 0.05 mol of monomer were emulsified in 80 mL of aqueous solution of SDS ($1.6 \cdot 10^{-3}$ mol), then 20 mL of previously aged (1 h at room temperature) aqueous solution of titanocene ($1.5 \cdot 10^{-5}$ mol) were added. After 2 h, the mixture was quenched in acidified methanol. The polymer was recovered by filtration, washed with fresh methanol, and dried at 40 °C in a vacuum oven.

2.3. Copolymerization

Styrene – 4-chloro-styrene (S-4CS) copolymers were prepared following the same procedure utilized for homopolymerizations, and by using mol quantities of styrene and 4-chloro-styrene in the feeding as reported in the following table.

| (S-4CS) sample | Styrene (mol) | 4-Chloro-styrene (mol) |
|----------------|---------------|------------------------|
| 1 | 0.044 | 0.042 |
| 2 | 0.025 | 0.033 |
| 3 | 0.021 | 0.013 |
| 4 | 0.022 | 0.051 |

2.4. Polymer analysis

^1H and ^{13}C NMR spectra were recorded on an AM 250 Bruker spectrometer operating at 62.89 MHz at 373 K. The samples were prepared by dissolving 40 mg of polymer in 0.5 mL of deuterated

tetrachloroethane ($\text{C}_2\text{D}_2\text{Cl}_4$). Hexamethyldisiloxane was used as internal chemical shift reference.

^2H spectra were recorded on a Bruker Advance 400 MHz spectrometer operating at 298 K. Samples were prepared by dissolving 20 mg of polymer in 0.5 mL of dichloromethane (CH_2Cl_2).

Infrared spectra were obtained at a resolution of 2.0 cm^{-1} with a Vector 22 Bruker spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm^{-1} using a He–Ne reference laser. Thirty-two scans were signal averaged to reduce the noise.

Calorimetric measurements were carried out on a DSC 2920 apparatus manufactured by TA Instruments, in flowing of nitrogen (N_2), with heating rate of $10 \text{ }^\circ\text{C}/\text{min}$.

Molecular weights (M_n and M_w) and molar mass distribution (MWD) of polymers were measured by gel permeation chromatography (GPC) at 30 °C, using THF as solvent, a flow rate of eluant of 1 mL/min and narrow polystyrene standards as references. The measurements were performed on a water 1525 binary system equipped with a water 2414 RI detector using four styragel columns (range 1000–1.000.000 Å).

3. Results and discussion

3.1. Styrene homopolymerization

Aqueous emulsion polymerization of styrene in the presence of half-titanocene leading a monoanionic monodentate ligand (CpTiCl_3), or a monoanionic bidentate ligand [$(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$], and of a titanocene leading a biantionic bidentate ligand $(\text{Ph})_2\text{C}[(\text{Cp})(\text{Flu})\text{Ti}]\text{Cl}_2$ (where: Cp = cyclopentadienyl, Flu = fluorenyl) compounds, were effected. All polymerization tests were carried out under nitrogen atmosphere in degassed water at 50 °C as already described by Bhattacharjee and Patra [32–34]. The used synthetic procedures are detailed in the experimental part.

In Table 1, experimental data relative to styrene polymerization tests are collected. For comparison, data relative to styrene polymerization are also reported.

Probably due to its poor solubility in water, titanocene $(\text{Ph})_2\text{C}[(\text{Cp})(\text{Flu})\text{Ti}]\text{Cl}_2$ does not show any activity in styrene polymerization. On the contrary, by using both half-titanocenes CpTiCl_3 and $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$, stereoirregular polystyrene, presenting the same features to that obtained by using Cp_2TiCl_2 , is produced. Polymer molecular weights up 10^6 Da, and polydispersity index values close 2.5 have been detected.

It is worth noting that, both CpTiCl_3 and $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$ present catalytic activity significantly lower than that showed by Cp_2TiCl_2 . In their reports, Bhattacharjee and coworkers suggested that Cp_2TiCl_2 , in water, undergoes hydrolysis producing, at least partially, the 14 electron rich cationic species $[\text{Cp}_2\text{TiOH}]^+$ [32,33] coordinatively unsaturated and that could be the true active catalyst responsible of styrene insertion polymerization. Styrene

Table 1
Styrene polymerization experimental data.

| Catalyst | Activity ^a g/(mol h) | M_w Da $\times 10^6$ | MWD ^b | T_g^c (°C) |
|--|------------------------------------|------------------------|------------------|--------------|
| $(\text{Ph})_2\text{C}[(\text{Cp})(\text{Flu})\text{Ti}]\text{Cl}_2$ | – | – | – | – |
| CpTiCl_3 | 2290 | 5.1 | 2.6 | 105 |
| $(\text{CpCH}_2\text{CH}_2\text{OCH}_3)\text{TiCl}_3$ | 339 | 4.3 | 2.4 | 104 |
| Cp_2TiCl_2 | 8200 | 5.4 | 2.4 | 105 |

^a A = activity = g of polymer/mol of Ti \times polymerization time (h).

^b Polydispersity index.

^c Glass transition temperature.

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