

Polyethylene-polyaniline Nanofiber Composites: Evaluation of Experimental Conditions of *in situ* Polymerization

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The difficult processability of polyaniline (PAni) can be overcome by preparing composites with high density polyethylene (HDPE), resulting in a conducting material with improved mechanical properties. PAni nanofibers were synthesized in this research using a rapid mixing method, while HDPE/PAni composites were prepared by *in situ* polymerization using $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ as a catalyst system. Different experimental conditions for polymerization and an electrochemical study were performed. The findings confirmed that the addition of small amounts of Pani (up to 7%) and longer impregnation (120 min) with methylaluminoxane (MAO) before polymerization are important factors contributing to increased catalytic activity. Analysis by cyclic and differential pulse voltammetry indicates that MAO reacts with the PAni in the ethylene polymerization process, and forms active species in the presence of the catalyst. Changes in catalytic activity may be due to the kinetic consumption of the active species, which become less important in the presence of PAni.

Keywords: polyaniline, polyethylene, cyclic voltammetry, composites

1. Introduction

Major advances have taken place in recent years in the technological application of conductive polymers thanks to their convenient processability. This has led to developments mainly in microelectronics and sensors, rechargeable batteries, electrochromic displays, light-emitting devices, and photovoltaic and insulation panels^{1,2}. Polyaniline (PAni) stands out among the conductive polymers due to its high electrical conductivity, chemical stability under ambient conditions, processability, ease of polymerization and doping ability, combined with low cost and low toxicity³. New methodologies have been developed within the past few years for the preparation of PAni-based nanostructures capable of dispersion, such as nanowires, nanofibers and nanotubes⁴.

PAni nanofibers can be prepared by rapid mixing, a simple and fast methodology that presents the advantage of not using organic solvent. However, applications of PAni have been limited due to its low solubility in common organic solvents and its difficult processability. This drawback can be overcome by the dispersion and formation of a conductive network of Pani nanofibers within conventional polymers, following different approaches

such as melt blending by extrusion, solution/dispersion, *in situ* polymerization, and electrochemical polymerization⁵. The principal advantages of these techniques lie in their easy up-scaling ability at relatively low cost. Few studies regarding *in situ* polymerization of ethylene in the presence of PAni have been reported in the scientific literature. Nonetheless, this method has been successfully applied to several types of particles (organomodified clays, carbon nanotubes, graphene sheets, etc.), leading to a more uniform dispersion of the nanoparticles within different polymer matrices, when compared to the direct dispersion attempts of neat particles^{6,7}.

PAni-filled polyethylene (PE/PAni) nanocomposites were successfully prepared by *in situ* polymerization of ethylene, directly catalyzed in the presence of PAni nanofibers. The catalyst system used was $[(\text{Cp})_2\text{ZrCl}_2]/\text{MAO}$. PAni nanofibers were found to significantly affect crystallization of the polyolefinic matrix, while preserving its thermal stability. A rise of catalytic activity by increasing the relative content of nanofibers was also observed. Measurement of the electrical properties showed that the PAni nanofibers were able to bring electro-conductive properties to the *in situ* polymerized PE/PAni nanocomposites. Such results

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are very promising in the search for new materials for engineering applications that require electrical conductivity⁸.

Cyclic and differential pulse voltammetry were employed in order to investigate the reactivity of Zr- and Ti alkoxide bidentate complexes in the presence of methylaluminoxane (MAO) and ethylene^{9,10}. The catalytic species resulting from the interaction between $[\text{Me}_2\text{Si}(\text{Cp})_2\text{ZrCl}_2]$ or $[\text{Cp}_2\text{ZrCl}_2]$ with MAO or trimethylaluminum (TMA) were also investigated by cyclic voltammetry¹¹. Furthermore, a series of metallocenes bearing different coordination spheres (Cp, MeCp, *n*-BuCp, *i*-BuCp, *t*-BuCp, Ind, IndH₁), bridges (Et, Me₂Si) and metal centers (Zr, Ti, Hf) were comparatively analyzed by voltammetry, and the correlation between electrochemical characteristics and catalysis activity evaluated¹²⁻¹⁴. Therefore, an understanding of the interaction between the $[\text{Cp}_2\text{ZrCl}_2]$ /MAO catalytic system and PANi can be substantiated by making use of pulse differential voltammetry.

PAni nanofibers were prepared in this work by the rapid mixing method and polyethylene composites by means of *in situ* polymerization. The ethylene polymerization process in the presence of nanofibers was studied through cyclic and differential pulse voltammetry in order to understand the interaction of the Cp_2ZrCl_2 /MAO/PAni catalytic system.

2. Experimental

2.1. Material

Aniline (Merck) was distilled in the presence of metallic zinc, as was toluene (F. Maya) with metallic sodium and benzophenone before their use. Ammonium peroxide disulphate (APS), hydrochloric acid (HCl) (Merck), methylaluminoxane (MAO) (10% by weight in toluene, Aldrich), dichlorobis(cyclopentadienyl)zirconium(IV), and $[(\text{Cp})_2\text{ZrCl}_2]$ (Sigma-Aldrich) were used as received. All manipulations for the synthesis of PE/PAni nanocomposites were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques.

2.2. Polyaniline nanofibers synthesis

Polyaniline nanofibers were prepared by rapid mixing synthesis, following the methodology proposed by Huang & Kaner¹⁵. The aniline polymerization was carried out at 60 °C. Ammonium peroxide disulphate (APS) was used as an oxidizing agent and hydrochloric acid (HCl) 1 mol.L⁻¹ as a dopant agent. The reaction yield was about 21%. In order to improve the removal of moisture and free dopant acid, the PANi nanofibers were washed repeatedly with a solution of water and acetone until pH 4. Then the sample was dried under vacuum in an oven at 80 °C for 30 hours.

2.3. PE/PAni nanocomposites synthesis

The polymerization reactions were carried in a 250 mL glass reactor. Dried toluene was used as a solvent, MAO as a cocatalyst, and $[(\text{Cp})_2\text{ZrCl}_2]$ as a catalyst (5×10^{-6} mol). For all polymerizations, MAO and $[(\text{Cp})_2\text{ZrCl}_2]$ were added in such a way that the $[\text{Al}]/[\text{Zr}]$ ratio was 1200. PANi nanofibers were overnight dried at 50 °C under reduced

pressure (ca. 5 mbars). Before the polymerization stage, dried PANi were sonicated (Unique Ultracleaner 1600A, 40 kHz) in toluene (20 or 60 min). Then a pretreatment was carried out by adding MAO and keeping it under mixing at 50 °C for a certain period of time (from 30 to 120 minutes). Next, $[(\text{Cp})_2\text{ZrCl}_2]$ was added and the mixture kept under stirring for 30 min. The ethylene polymerization were carried out at 50 °C for 12 minutes by using different ethylene pressure (2.0 or 2.8 bars). After polymerization, the reaction mixture was dispersed in 7 volumes of methanol acidified with few drops of HCl aqueous solution (1 mol.L⁻¹) and nanocomposites recovered by filtration.

2.4. Differential pulse voltammetry (DPV)

The pulse differential voltammograms were taken with a potentiostat/galvanostat (PARC, model 273). All experiments were carried out using a conventional three electrode cell. Glassy carbon was used as the working electrode and another electrode was built from a PVC body having a graphite disk, which supports a carbon paste. Carbon paste was prepared by mixing high purity graphite (100 mg) (Fisher Scientific) and the polyaniline (30 mg) with a few drops of mineral oil. An Ag/AgCl electrode was used as a reference electrode and a platinum wire as an auxiliary electrode. The Ag/AgCl electrode was calibrated with ferrocene, which was used as an internal reference. These measurements versus the ferrocene (Fc⁺/Fc⁰) redox couple (+0.45 V in acetonitrile solutions) were reported against an Ag/AgCl electrode. Electrochemical data was attained by using 0.1 mol.L⁻¹ solutions of tetrabutylammonium tetrafluoroborate in acetonitrile as a supporting electrolyte. All solutions were deaerated by bubbling with high purity argon. The cocatalyst solutions were prepared with different $[\text{Al}/\text{Zr}]$, 3 and 6 ratios and the pulse voltammograms were recorded with a scan rate of 100 mV.s⁻¹.

2.5. Polyaniline nanofibers and composites based on PE/PAni characterization

Scanning Electron Microscopy (SEM) was carried out with the use of a Hitachi SU8020 model microscope, operating at 1.5 kV. Electrical conductivity measurements were carried out on samples in the form of pellets (13mm diameter by 2mm thick) using a Keithley Multimeter - Multimeter / Switch System Integra Series, Model 2750.

3. Results and Discussion

3.1. Polyaniline nanofiber synthesis

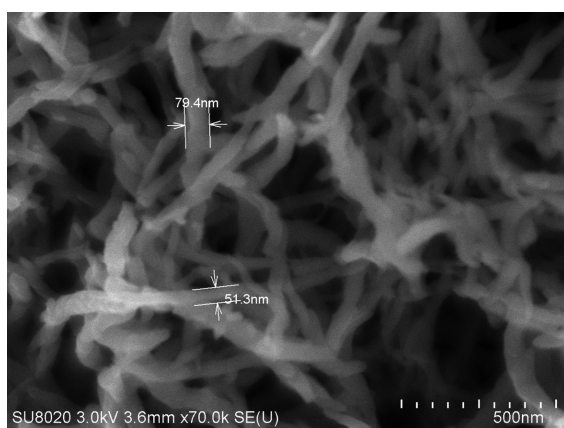
PAni nanofibers were synthesized via the rapid mixing method, which entails the aniline and oxidizing agent (APS) being mixed rapidly in the presence of the dopant (HCl). All the reagents in this process are considered to be consumed in the initial formation of nanofibers, thus preventing secondary growth that would result in the formation of particulate PANi^{5,16}. The main advantage of this procedure over interfacial polymerization is the absence of a solvent as a reagent. A washing step to pH 4 and oven-drying were then carried out to remove

excess dopant and residual moisture in order to prevent deactivation of the catalyst system during the *in situ* ethylene polymerization stage⁸.

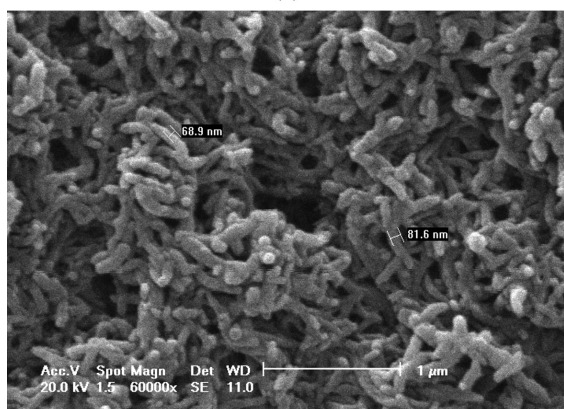
Typical SEM images of the synthesized PANi nanofibers are shown in Figure 1. Nanofibers characterized by high aspect ratio proved to form a largely interconnected network.

PAni conductivity is dependent on the concentration and mobility of charges (electron migration along the polyaniline chain), which in turn depends on the type of dopant, preparation method and structure of the doped PANi¹⁷.

Preparation of the PANi nanofibers by the rapid mixing method was found not to have significantly changed the morphology and electrical conductivity of the nanofibers after the pretreatment step, as seen in Figure 1b and Table 1.



(a)



(b)

Figure 1. SEM of polyaniline nanofibers: (a) untreated polyaniline (b) treated polyaniline.

Table 1. Electrical properties of polyaniline nanofibers treated and untreated.

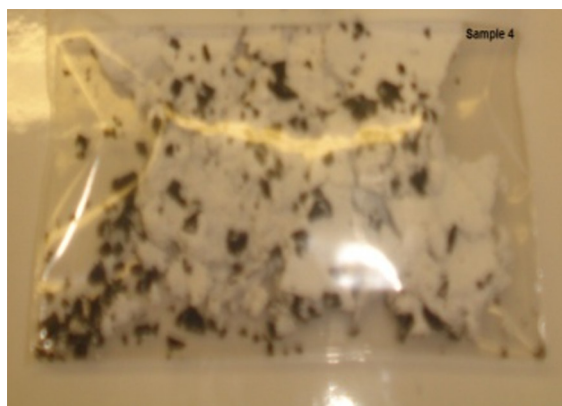
Sample	pH	Vacuum oven	Electric Resistivity (Ω.cm)
Untreated PANi	2.0	--	30.5
Treated PANi	4.0	T=80 °C, 30 hours	45.5

3.2. Synthesis of PE/PAni composites

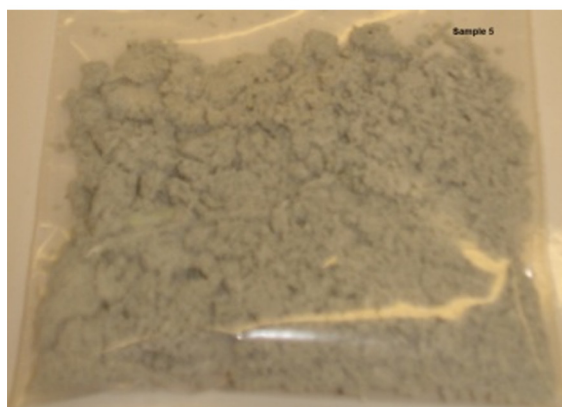
The polyethylene and PANi nanofiber composites with different amounts of filler were obtained by *in situ* ethylene polymerization using the [Cp₂ZrCl₂]/MAO catalytic system. Disaggregation of the nanofibers in toluene by a sonication step was first required in order to achieve their good dispersion within the polyethylene matrix. Figure 2 highlights that the longer the sonication step, the more homogeneous will be the final composite morphology.

The influence of the experimental conditions (amount of PANi, ethylene pressure, and MAO quantity) on catalytic activity were evaluated in order to gain a better understanding of the process of polymerizing ethylene in the presence of PANi nanofibers. Table 2 presents the catalytic activity results in this process using the [Cp₂ZrCl₂]/MAO catalytic system.

The presence of PANi was found to increase the catalytic activity of the system, as seen in Table 2 under the evaluated conditions. However, an excess of PANi appears to lead to its decrease (samples 1, 2 and 6). Moreover, longer pre-contact between the PANi and MAO before polymerization would seem to have a positive influence on the catalytic activity



(a)



(b)

Figure 2. PE/PAni composites. Influence of sonication time of the nanofibers in toluene before polymerization: (a) 20 minutes (b) 60 minutes.

Table 2. Catalytic activity in ethylene polymerization under different experimental conditions.

Sample	PAni (g)	Ethylene Pressure (bar)	MAO (mL)	Catalytic Activity (kgPE/molZr.h.bar)
1	--	2.8	3.6	252.2
2	0.25	2.8	3.6	1183.7
3 ^a	0.25	2.8	1.8	1307.3
4	0.25	2.8	1.8	849.1
5	0.25	2.0	3.6	1224.1
6	0.50	2.8	3.6	507.8

^aPAni pre-contact with MAO in toluene for 120 min.

of the system (samples 3 and 4). A theory to explain such a result depends on the ability to generate interactions between the PAni and $[(Cp)_2ZrCl_2]/MAO$. An electrochemical investigation was performed to further strengthen this idea and identify their nature, with the results described in the following section.

It is also noteworthy that the ethylene pressure had no significant influence on the catalytic activity (samples 2 and 5).

3.3. Differential pulse voltammetry (DPV)

Figure 3 (curve a) shows the differential pulse voltammogram with cathodic scan for the PAni-modified electrode, which exhibited a cathodic peak at -1.35 V. This polymer presented no sign when dispersed in the solution and not as part of the electrode composition. Consequently, it can be asserted that PAni is a conductor system.

Figure 3 (curve b) illustrates the cathodic signs to the metallocene complex $[(Cp)_2ZrCl_2]$ used as a catalyst in the catalytic system PAni/ $[(Cp)_2ZrCl_2]/MAO$. The differential pulse voltammogram illustrates cathodic signs at -1.55 V, -1.75 V and -2.0 V, which were attributed to the redox process centered on the metallic ion¹¹.

In order to understand curve c in Figure 3, it is necessary to evaluate the profile of the differential pulse voltammogram for $[(Cp)_2ZrCl_2]$ with an anodic and cathodic sweep in Figure 4. Negative potentials show three redox pairs assigned to the reduction of zirconium (Figure 4 - curves a and b-1). Besides these peaks there is an irreversible anodic process at a positive potential that involves ligand oxidation (Figure 4 - curve b-2).

Taking into account the $[(Cp)_2ZrCl_2]$ data in Figure 3 (curve b), the pulse differential voltammetry profile in a cathodic scan of the PAni/ $[(Cp)_2ZrCl_2]$ modified electrode (Figure 3-curve c) shows the presence of a large sign in the -1.5 V region, which is assigned to the reduction/oxidation of zirconium with the contribution of PAni reduction (Figure 3 - curve b). Two additional reductions at a more negative potential with low current intensity were illustrated and are attributed to other reductions of the metallic center.

The differential pulse voltammogram in Figure 5 of $[(Cp)_2ZrCl_2]$ in acetonitrile solutions in the presence of PAni illustrates a small shift of the cathodic peaks attributed to the reduction of Zr, but the numbers of sign $[(Cp)_2ZrCl_2]$ in acetonitrile solution with the absence of PAni are equal. This suggests similar stability for Zr(IV). These results

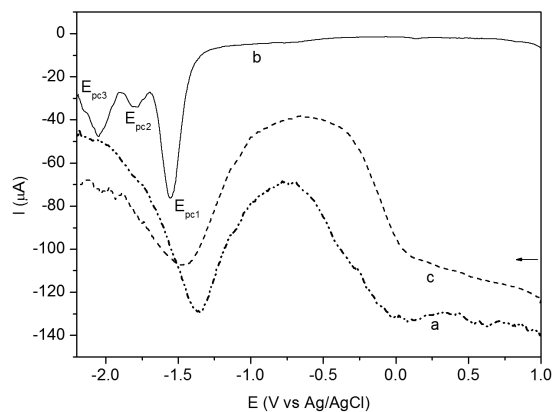


Figure 3. Differential pulse voltammograms – (a) polyaniline-modified electrode (b) $1 \times 10^{-3} \text{ mol L}^{-1} [(Cp)_2ZrCl_2]$ and (c) PAni/ $[(Cp)_2ZrCl_2]$ -modified electrode. $v = 100 \text{ mV s}^{-1}$.

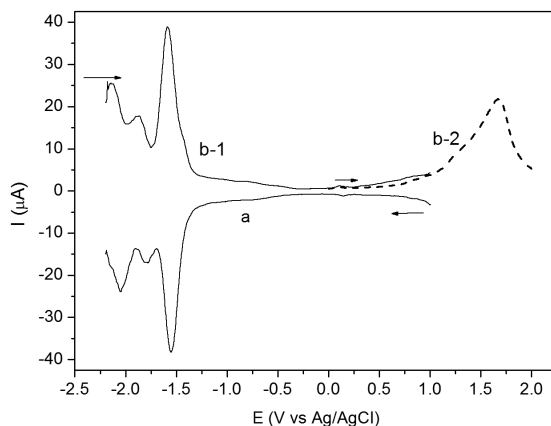


Figure 4. Differential pulse voltammograms of $1 \times 10^{-3} \text{ mol. L}^{-1} [(Cp)_2ZrCl_2]$ $v = 100 \text{ mV.s}^{-1}$. (a) cathodic scan and (b) anodic scan.

are consistent with a weak interaction between PAni and metallocene.

The electrochemical behavior of PAni/ $[(Cp)_2ZrCl_2]$ was also investigated in the presence of MAO. Figure 6 shows the DPV of $[(Cp)_2ZrCl_2]$ with amounts of MAO in a molar ratio Al/Zr = 3 and 6. The successive pulse voltammograms show that the current of the cathodic peak centered at -1.5 V (E_{pc1}) disappeared and for E_{pc2} the intensity current

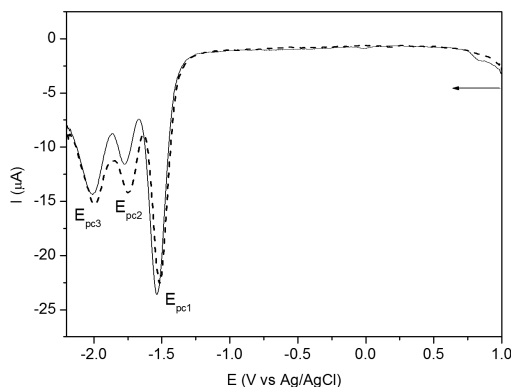


Figure 5. Differential pulse voltammograms of 1×10^{-3} mol. L $^{-1}$ $[\text{Cp}_2\text{ZrCl}_2]$ $v = 100$ mV.s $^{-1}$. Cathodic scan. Curve (solid): $[\text{Cp}_2\text{ZrCl}_2]$ in acetonitrile solution. Curve (dash): $[\text{Cp}_2\text{ZrCl}_2]/\text{PANI}$ in acetonitrile solution.

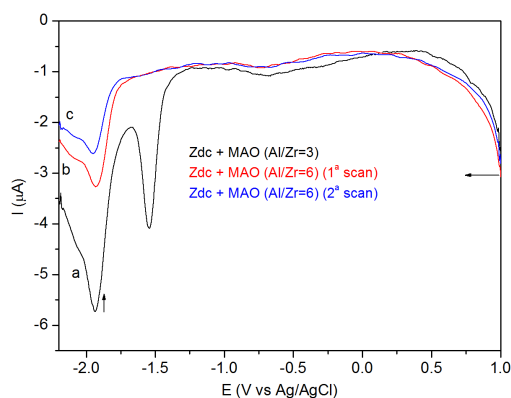


Figure 6. Differential pulse voltammograms of 1×10^{-3} mol. L $^{-1}$ $[\text{Cp}_2\text{ZrCl}_2]$ with MAO. Al/MAO: 3 (a), 6 (b) (first scan), and (c) (second scan). Cathodic scan. $v = 100$ mV.s $^{-1}$.

decreased within time. Silveira and coworkers reported that this fact is related to the possible instability of the species containing the methyl group which is active in the polymerization reaction¹². On the other hand, the DPV PANi/ $[\text{Cp}_2\text{ZrCl}_2]/\text{MAO}$ can be seen in Figure 7 in which the consumption of $[\text{Cp}_2\text{ZrCl}_2]$ for the formation of active species occurs in a longer period if compared to the absence of PANi (Figure 6), which is probably due to part of the consumption of MAO by PANi.

Therefore the increase of catalytic activity may be a kinetic consequence of the consumption of the active

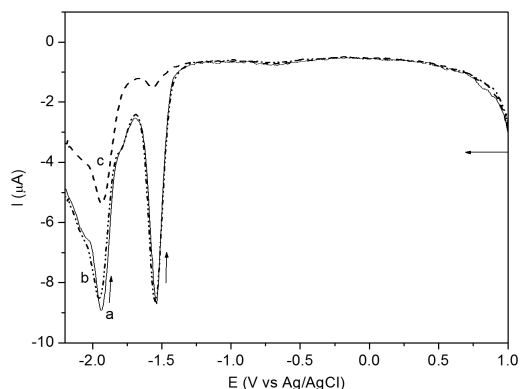


Figure 7. Differential pulse voltammograms of 1×10^{-3} mol L $^{-1}$ $[(\text{Cp})_2\text{ZrCl}_2]$ with PANi/MAO. Al/Zr: 3 e 6. $v = 100$ mV.s $^{-1}$. Cathodic scan (a) Al/Zr=3 (first scan), (b) Al/Zr=3 (second scan), (c) Al/Zr=6.

species, which is lower with the presence of PANi. However, an excess of PANi in the reaction medium may cause the MAO to become unavailable for the formation of the active species and thus diminish catalytic activity.

4. Conclusions

PANI nanofibers and polyethylene composites were prepared by *in situ* ethylene polymerization. Pretreatment for excess moisture and dopant removal did not significantly alter the morphology and electrical conductivity of the nanofibers. The catalytic activity of the MAO/ $[\text{Cp}_2\text{ZrCl}_2]$ system was notably affected by the amount of PANi nanofibers present in the reaction medium during the ethylene polymerization. Electrochemical study showed that catalytic alteration may be due to kinetic consumption of the active species, which occurs at a lower rate in the presence of polyaniline. The polymerization reaction step involving coordination of the ethylene to the metallic center of the active species is more favored as the PANi/ $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalytically active species has a longer half-life, justifying the increased catalytic activity. This statement is based on the negligible change in the Zr^{IV/III} reduction potential of pure $[\text{Cp}_2\text{ZrCl}_2]$ and in the catalytic system in the presence of PANi.

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