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Synthesis of semiconducting polyphenylacetylene catalyzed by $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$

Adriane S. Gruber[1], Gisèle Boiteux[2], Roberto F. de Souza , Michèle O. de Souza (✉)

Universidade Federal do Rio Grande do Sul, Instituto de Química, Av. Bento Gonçalves 9500,
91501-970, P.O. Box 15003, Porto Alegre, Brazil
[1]Pontífica Universidade Católica do RGS, Faculdade de Química, Predio 12,
Av. Ipiranga 6681, 90619 900 Porto Alegre, Brazil
[2] UMR 5827, LEMPB ISTIL, Domaine Scientifique de la Doua, 43 boulevard du 11 Novembre 1918,
F-69622 Villeurbanne Cedex , France

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Summary

Phenylacetylene (PhA) is polymerized by the dicationic nickel complex $Ni(MeCN)_6(BF_4)_2$ associated with $AlEt_2Cl$ as co-catalyst. The production of 200g of polymer per gram of nickel per hour represents a typical activity of this system. Under our experimental conditions, the polymer displays an exclusive *trans* structure. The molecular weight distribution of the polymer is polymodal (5000 $g.mol^{-1}$ and 200 $g.mol^{-1}$). The highest average molecular weight fraction (5000 g. mol^{-1}) represents the highest published value for polyphenylacetylene (PPA) where a nickel catalyst is employed. The electrical conductivities vary between 10^{-7} and 10^{-16} $S.cm^{-1}$, and are characteristic of a semi-conductor polymer. Equivalent values are cited in the literature only in the case of doped PPA. Experimental observations enabled us to propose a mechanism for the formation of the active species through the reaction of $Ni(MeCN)_6(BF_4)_2$ with $AlEt_2Cl$.

Introduction

Organic polymers displaying electrical conducting properties constitute an interesting class of materials for technological applications [1]. The synthesis of such polymers from acetylene (leading to a polymer with conjugated carbon-carbon double bonds) produces material with satisfactory conducting properties (10^{-4} $S.cm^{-1}$ for doped *trans*-polyacetylene) although these polymers are unstable in air and show low solubility in common solvents. Substituted polyacetylene polymers are stable in air but display low conducting values (*ca.* 10^{-15} to 10^{-18} $S.cm^{-1}$). Their stability is due to the tri-substituted C=C bonds, which are less reactive than their double-substituted counterparts. The presence of substitutents along the chain leads to steric hindrance and this determines deviations from a planar structure that decrease π electron delocalization. The loss of such delocalization has many consequences, such as a variation in the color (polyacetylene is dark gray and poly-*t*-butylacetylene is white) and also a change in electrical conductivity (10^{-4} $S.cm^{-1}$ for polyacetylene and 10^{-15} $S.cm^{-1}$ for poly-*t*-butylacetylene). Polyphenylacetylene seems to be an exception in this context. The chemical and physical properties of this material are intermediate compared with polyacetylene and other substituted polyacetylenes. Its color can vary from red-brown to yellow, it is soluble in common organic solvents such as toluene, dichloromethane and acetone, is stable in air and displays semi-conductor properties (10^{-10} $S.cm^{-1}$), which is *ca* 10^{8} fold more conducting than polystyrene, which is the corresponding non-conjugated structure [2]. Tkatchenko *et al.* synthesized a semi-conductor polyphenylacetylene using $[Ni(\eta^3\text{-allyl})(\eta^4\text{-1,5-cyclooctadiene})]PF_6$ as polymerization catalyst [3]. These authors showed that, depending on the experimental conditions, the proportion of *cis / trans* polymer changes and the conductivity properties are modified. When the *cis* configuration is predominant, the conductivity values are *ca.* 10^{-16} $S.cm^{-1}$, and when the majority of the polymer show a *trans* configuration, the conductivity values attain 10^{-6} to 10^{-7} $S.cm^{-1}$ [2,4]. We have described the complex $Ni(MeCN)_6(BF_4)_2$ associated with $AlEt_2Cl$, which is a new outstanding catalytic precursor for ethylene and propylene oligomerization [5]. Thereafter we decided to study the catalytic properties of this system for the polymerization of phenylacetylene, and these results are reported herein.

Experimental

Materials

All manipulations were performed using standard Schlenk tube techniques under dry argon. Solvents were distilled over desiccants immediately before use. The complex *bis*(tertrafluoroborate) nickel hexaquis(acetonitrile) ($Ni(MeCN)_6(BF_4)_2$) was synthesized as previously described [6].

Polymerization

To a catalyst solution containing 0.06 mmol of $Ni(MeCN)_6(BF_4)_2$ in 15 mL of toluene, dichloromethane or chlorobenzene, prepared in a 250 mL Schlenk tube, is added 45.5 mmol of phenylacetylene. A 1.8 M solution of diethylaluminum chloride ($AlEt_2Cl$) is introduced in order to obtain a defined value for the aluminum to nickel molar ratio and the temperature was controlled by an external circulation bath. At the end of the reaction time (1, 3, 6 or 17 hours) the solvent is evaporated under reduced pressure. From the weight of the dried product the catalytic activity as a turnover frequency is calculated (moles of phenylacetylene to moles of nickel and per hour). Selected samples has been submitted to recrystalization from dichloromethane and methanol in order to obtain pure polymers for electrical conductivity measurements.

Kinetic study

The conversion of 8 mmol of phenylacetylene in 15 mL of solvent (toluene, chlorobenzene or dichloromethane) is observed through gas chromatographic analysis when 1mL of $AlEt_2Cl$ (molar ratio Al/Ni = 25) is added in the presence of 0.6 mL of cyclohexane as internal standard.

Electrical properties

The electrical conductivity has been determined at room temperature by a technique leading to bulk conductivity value measuring the intensity for a given voltage [7]. The samples are sintered pellets of different thickness (e = 0.5 –1 mm) and constant diameter (D = 11,3 mm) obtained after degassing by compressing the polymer powder under 8000 bars over 15 min at room-temperature. The disk is placed in a thermoregulated cell between two electrodes. Variable electrical fields up to 50 V (DC), are applied and the evolution of the corresponding intensity versus time (5 hours) is measured with a Keithley 617 electrometer, respectively for insulators and semi-conducting materials, the frontier value being 10^{-9} A. Coupling with an Apple II C microcomputer leads to a graph where the constant limit value of current allows the determination of conductivity σ ($\sigma = Ie/(\pi V D^2)$) in $S.cm^{-1}$. Measures are repeated at least three times on different disks of a given polymer.

Results and Discussion

Phenylacetylene (PhA) is polymerized, in the homogeneous phase, by $Ni(MeCN)_6(BF_4)_2$ combined with $AlEt_2Cl$. Conversion data are obtained through the determination of the consumption of PhA against the reaction time, with turnover frequency (TOF) being calculated from the mass of polymer produced per mol of nickel complex and per hour of reaction.

The polarity of the solvent influences the conversion of the phenylacetylene [4,8]. Ziegler-Natta systems are favored by polar solvents [8a,b] in accordance with the fact that ionic moieties are the catalytically active species as suggested by Siskos *et al.* [8b]. The polymerization of PhA by nickel/alkylaluminum (Ni/Al) has been performed using chlorobenzene (PhCl), dichloromethane (CH_2Cl_2) and toluene (PhMe) as solvent, in order to evaluate the influence of the polarity of the solvent on our reaction system. Figure 1 shows the conversion results obtained as a function of time for the reaction performed with different solvents under the same reaction conditions (Al/Ni) =25; (PhAc/Ni) = 150; temperature = 25 °C). For all solvents, the conversion increases rapidly initially and attains a limit after one hour. Similar plateaus have already been reported but not justified [8a,b]. We suggest that, in our case, this phenomenon corresponds to a deactivation process. The best conversion is observed for chlorobenzene, the most polar solvent, indicating the best stabilization effect of the catalytic species by this solvent. The inversion of the order of best conversion and polarity of the solvent observed for PhMe and CH_2Cl_2 can be explained by the reaction of the alkylating agent with CH_2Cl_2, as illustrated in the following sequence of reactions [9].

$$AlEt_2Cl + CH_2Cl_2 \rightarrow AlEtCl_2 + EtCH_2Cl \qquad (\mathbf{1})$$
$$AlEtCl_2 + CH_2Cl_2 \rightarrow AlCl_3 + EtCH_2Cl \qquad (\mathbf{2})$$

Previous studies on the oligomerization of ethylene catalyzed by $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$ have shown that the value of the molar ratio between the co-catalyst and the nickel complex, Al/Ni, influences the product distribution [5].

The influence of the Al/Ni ratio for the polymerization of phenylacetylene has been investigated. Figure 2 shows the evolution of the turnover frequency with (Al/Ni) ratio at 25°C.

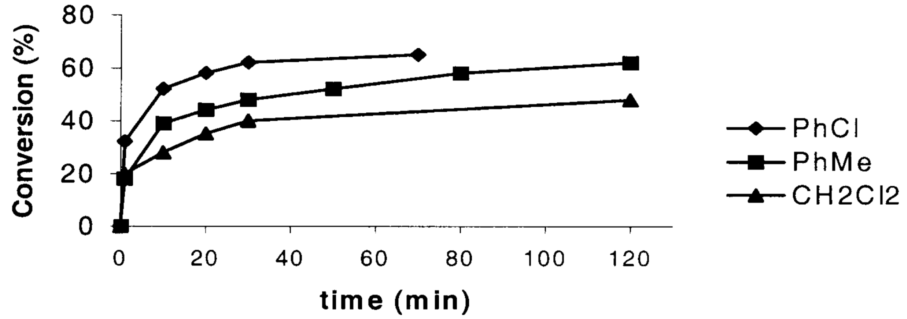

Figure 1. Influence of the nature of the solvent on the conversion of PhA measured as a function of time. Catalyst system: $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$, Temperature: 25 °C

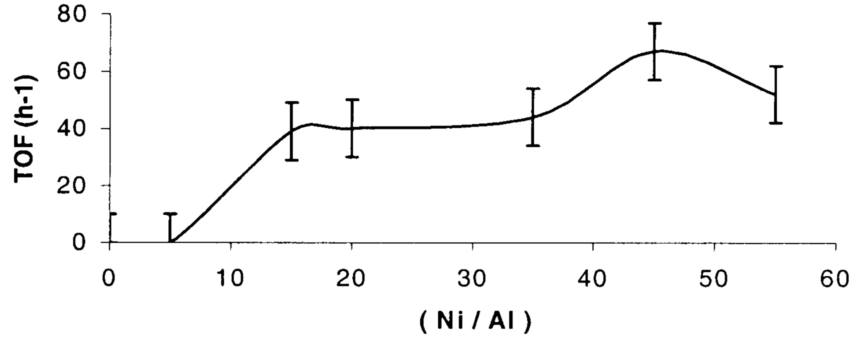

Figure 2. Influence of the molar ratio Ni/Al on the activity of the $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$ catalyst system for PhA polymerization. Temperature 25 °C, solvent: toluene

This shows that a minimal quantity of co-catalyst has to be added to generate an active species for PhA polymerization (when Al/Ni = 5, TOF = 0). It is known that acetonitrile ligands coordinated to nickel react with the alkylaluminum compound [9], liberating vacant sites on the metal. This reaction between the nickel complex and the co-catalyst explain that a minimal quantity of $AlEt_2Cl$ is necessary and also that the activity shows a maximal value when Al/Ni increases. The form of the curve herein obtained is typical of several Ziegler-Natta systems, and characterizes the well-known sensitivity of such systems relating to the Al/Ni parameter [10].

The influence of different reaction parameters on the nature, structure and conductivity properties of the reaction product of the PhA polymerization with $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$ has been investigated. The analyses by gel permeation chromatography (GPC) show polymodal distributions, independent of the modification of the reaction parameter. A typical GPC trace (elution volume (V_E) versus Absorbance) is showed in Figure 3a. These GPC analysis shows three major areas: (i) at $V_E \cong 15$ mL corresponding to polymer of $\overline{Mn} = 5000$ g.mol^{-1}; (ii) with V_E between 17 and 22 mL, corresponding to material with $\overline{Mn}$ between 2300 and 300 g.mol^{-1} and (iii) $V_E = 23$ mL corresponding to $\overline{Mn} = 200$ g.mol^{-1}, *i.e.* dimers. It is worth to note that the intermediary fraction ($\overline{Mn}$ between 2300 and 300 g.mol^{-1}) contains peaks corresponding to trimers ($V_E = 22$ mL) and tetramers ($V_E = 21.5$ mL). These products are expected to be formed by different mechanisms, as previously described by Meriwether *et al.* [11]. Differently from nickelocene catalysts [12, 13] our system conducts to dimers (V_E = 23 mL), trimers (V_E = 22 mL) and tetramers (V_E = 21.5 mL), unambiguously identified in this GPC trace. Complementary GC and GPC analyses with co-injection of PhA showed no monomer mixed with oligomers. It should be mentioned that alkylaluminum compounds are known to be active in PhA oligomerization [14]. Control tests performed with $AlEt_2Cl$, without nickel complexes, gave products with molecular weights from 300 to 2300 $g.mol^{-1}$, as shown in curve 3b (V_E between 17 and 23 mL).

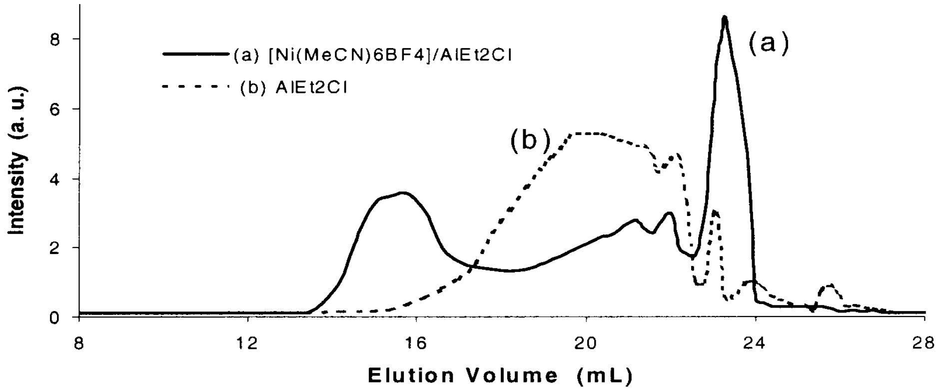

Figure 3. GPC distribution curves of reaction product from PhA converted by $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$ or $AlEt_2Cl$. Temperature: 25 °C, Solvent: toluene

The superimposition of the two analysis (with $Ni(MeCN)_6(BF_4)_2$/ $AlEt_2Cl$ with Al/Ni = 15 (figure 3) shows that the excess $AlEt_2Cl$ is responsible for the formation of the low molecular-weight polymers and oligomers and that the active species generated by the association of $Ni(MeCN)_6(BF_4)_2$ with $AlEt_2Cl$ should be responsible for the formation of dimers and the high polymers. The polymer ($\overline{Mn}$ = 5000 $g.mol^{-1}$) corresponds to chains containing in average 49 monomer units. It is interesting to mention that, as far as we know, the highest molecular weight polyphenylacetylene has been produced by a nickelocene complexes ($\overline{Mn}$ = 3000 $g.mol^{-1}$) [12] and that polyphenylacetylene produced by other known nickel systems have average molecular weight lower than 2000 $g.mol^{-1}$ [2,3].

Table 1 reports polymer selectivity results (S_P) that represent the fraction of polymer with $\overline{Mn} \cong 5000$ $g.mol^{-1}$ in the reaction products obtained in the total quantity of product formed. Experimental parameters have been specifically studied such as: nature of the solvent (CH_2Cl_2, PhMe and PhCl), relative concentration of PhA to the catalyst precursor (PhA/Ni), relative concentration of co-catalyst to the catalyst precursor (Al/Ni) and reaction temperature. Runs (1-3) were performed with a low monomer concentration (PhA/Ni = 100 – 150) with a constant concentration of alkylaluminum co-catalyst at Al/Ni = 25 and a reaction temperature of 25° C.

The higher selectivity in polymer is obtained with toluene (run 2, S_P = 65 %). With CH_2Cl_2 as solvent (run 1), this selectivity drops to 37%, which corroborates that there is a parallel reaction between the solvent and $AlEt_2Cl$ leading to the formation of $AlCl_3$ as mentioned above. The $AlCl_3$ generated *in-situ* is responsible for the formation of a higher proportion of low molecular weight products. Based on the similarity of the results when CH_2Cl_2 and PhCl are used, one can speculate that the same phenomenon occurs with PhCl. We have carried out complementary reactions with variable concentrations of PhA in PhMe and PhCl (Table 1, runs 4 and 5, PhA/Ni = 780 and 668 respectively, at Al/Ni =25 and T =25° C). Comparing S_P values of run 2 to run 4 (S_P drop from 65 to 20 %) and of run 3 to run 5 (S_P drop from 30 to 23%) we can deduce that the increase in the proportion of PhA to Ni prevents the formation of high molecular weight polymers. One can propose that the active species from $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$ produces a long chain polymer. When there is an excess of PhA (high PhA/Ni ratio) the monomer reacts with the alkylaluminum compound leading to low molecular weight polymer or oligomers. These parallel reactions contribute to the decrease of the proportion of polymer as shown by the S_P results of the Table 1. Further experiments (runs 6 to 8) have been performed using PhMe as solvent with quantities of co-catalyst increasing with respect to the catalytic precursor (Al/Ni = 15, 45 and 55) to investigate the influence of $AlEt_2Cl$ on the formation of low molecular weight polymers.

When PhMe is used as solvent, and for a similar monomer concentration (PhA/Ni *ca.* 780) we observe that the best Al/Ni ratio to obtain a high polymer is 15 (comparing runs 4, 6 ,7 and 8). When the alkylaluminum amount increases the proportion of high polymer decreases. This is explained by the fact that the excess of $AlEt_2Cl$ produces low molecular weight polymer.

Table 1. Influence of reation parameters (solvent, (PhA/Ni) and (Al/Ni) molar ratio) on the nature and conductivity properties of product of PhA polymerization

Run	Solvent	PhA/Ni	Al/Ni	S_P (%)	σ ($S.cm^{-1}$)
1[(a)]	CH_2Cl_2	136	25	37	$1.4\ 10^{-7}$
2[(a)]	PhMe	148	25	65	$6.9\ 10^{-10}$
3[(a)]	PhCl	101	25	30	$5.7\ 10^{-10}$
4[(a)]	PhMe	780	25	20	
5[(a)]	PhCl	668	25	23	
6[(b)]	PhMe	778	15	30	$1.8\ 10^{-8}$
7[(b)]	PhMe	770	45	19	$2.7\ 10^{-10}$
8[(b)]	PhMe	780	55	23	
9[(c)]	PhMe	720	25	51	

Temperature (a) and (b) = 25 °C, (c) = -20 °C; time (a) = 17 hours, (b) = 6 hours, (c) = 1 hour

Reaction 9 is performed at –20°C to minimize the possibility of thermal deactivation of the active species. As the results of Table 1 show, even with a high quantity of PhA (PhA/Ni = 720), the second best proportion of high polymer has been obtained (S_P = 51%). This result suggests that low temperature minimizes deactivation of the active species responsible for the polymerization and/or avoids the parallel reaction of $AlEt_2Cl$ that leads to the formation of low polymer or oligomers.

The analyses of the polyphenylacetylene by IR show that the product obtained has a *trans* configuration evidenced by the intense absorption at 755 and 700 cm^{-1} ($\delta(C{-}H)_{aromatic}$). These absorptions are characteristic of a phenyl group in a *trans* position with regard to the hydrogen of the double C=C bond and the absence of any absorption at 740cm^{-1} confirms that no *cis* isomer is formed [15].

Table 1 reports the results of the conductivity (σ) of the polyphenylacetylene obtained under different experimental conditions.

Before commenting on these conductivity results it is important to recall that a conductivity of *ca.* 10^{-7} $S.cm^{-1}$ characterizes a semi-conductor material and less than 10^{-9} $S.cm^{-1}$ an insulator. The results in Table 1 show that a semi-conductor polymer is obtained when the polymerization is performed in CH_2Cl_2. For the other solvents tested herein (PhMe and PhCl), the reaction product is an insulator.

In the case of the polyacetylene, the conductivity of the polymer is due to the formation of *solitons* which are radicals associated with defects in the polymerization process. These *solitons* can move along the polymer chain only when the structure of the polymer has a *trans* configuration [16]. Such phenomena can explain why only for doped *trans*-polyacetylene, the conductivity can attain 10^{-2} $S.cm^{-1}$ [3,17]. Based on this model, we can propose that CH_2Cl_2 favors defects of the process of the polymerization leading to the formation of a high quantity of radicals responsible for the highest value of the conductivity of the polyphenylacetylene. Observing the results of conductivity of the reactions 2, 6 and 7, where the solvent is PhMe and the Al/Ni ratio is 15, 25 and 45 respectively, we can see that an excess of $AlEt_2Cl$ does not favor the formation of a conducting material. Even if the proportion of high polymer increases (increase of Al/Ni from 15 to 25 lead to S_P equal to 65 and 30 % respectively), the conductivity decreases from 1.8 10^{-8} to 6.9 10^{-10} $S.cm^{-1}$.

As we have already mentioned, the conversion of the polymerization increases with the polarity of the solvent. This result indicates that the polymerization of the phenylacetylene involves cationic species as Siskos *et al.*[8c] suggest for the same polymerization catalyzed by a hafnium complex associated with an alkylaluminum agent. The authors showed that conversion is increased when a polar solvent is used. We propose that the active species is generated by the reaction between $[Ni(MeCN)_6]^{2+}$ and $AlEt_2Cl$ through a coordination mechanism. The early stages of this reaction are (Figure 4): coordination of the alkylaluminum compound to the nickel through the electron pair of the chlorine atom, transalkylation and β-elimination. The coordination of the $AlEt_2Cl$ molecule to the nickel is enabled by the reaction of a MeCN ligand with $AlEt_2Cl$ in excess leading to the formation of the adducts $ClEt_2Al$:CNMe [9]. The formation of a bi-metallic complex is evidenced by the modification of the color of the system when $AlEt_2Cl$ is added to $Ni(MeCN)_6(BF_4)_2$ [3,18]. As the thermodynamic stability of the C-Al bond is lower than of that of a C-Ni bond, the transalkylation stage is favored [19]. The active species formed in this process, which is a nickel hydride, is generated by the β -elimination of an ethylene molecule. This step is supported by the observation of ethylene (through gas chromatographic analysis).

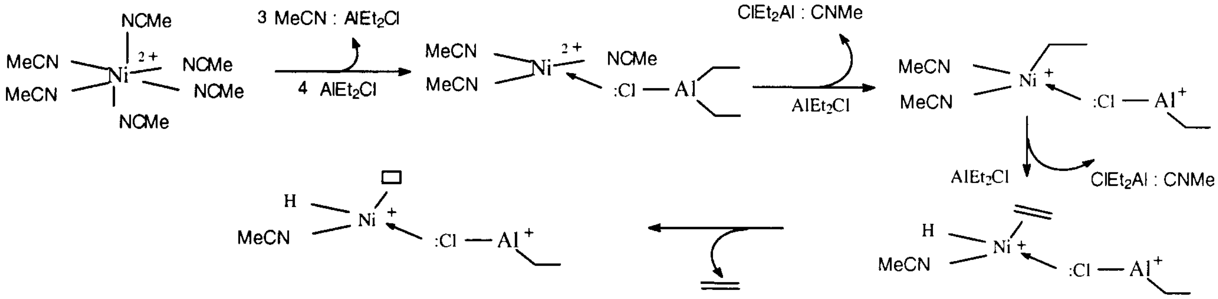

Figure 4. Mechanism of the formation of the catalytic active species from $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$

It is worth noting that the reaction of an alkylaluminum with phenylacetylene leads only to the evolution of ethane [20]. To certify that the detected product was ethylene, in the case of the generation of the catalytic species, and not ethane, we have performed the reaction between phenylacetylene and $AlEt_2Cl$. The detected product was exclusively ethane. The identification of ethylene represents important evidence that the active species in this system are cationic nickel hydride complexes formed as illustrated in Figure 4. Control runs showed that diphenylacetylene is not polymerized with the system $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$. This suggests that the polymerization mechanism includes an acetylene hydrogen transfer step as proposed by Meriwether [11,12].

Conclusion

The $Ni(MeCN)_6(BF_4)_2/AlEt_2Cl$ system is active for the catalytic polymerization of PhA. Evidence has shown that the catalytic species are cationic and are stabilized by polar solvents. These active species are responsible for the production of *trans*-polyphenylacetylene containing 45 to 65 monomer units and an excess of PhA and/or $AlEt_2Cl$ favored the production of low molecular weight polymer and oligomers. When the solvent is $CHCl_2$ the material shows highly conductive properties probably due to the presence of high quantities of solitons. The formation of cationic active species has been evidenced and a mechanism for their formation is proposed.

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