

Maghnite-H⁺ catalytic synthesis and characterization of Polyindenes and oxidized derivatives

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Abstract

This work presents a comprehensive study on the physico-chemical and electrochemical properties of polyindenes (PIs) synthesized by Maghnite-H⁺-catalysed polymerization of indene (In) in CH₂Cl₂ at different temperatures, and their oxidative derivatives (PIOs) by subsequent treatment with FeCl₃. The PIs and PIOs were thoroughly characterized by different techniques, such as thermogravimetry (TG), FT-IR, XPS and UV-vis spectroscopies, as well as electrical conductivity and voltammetric measurements, analysing the influence of both the temperature of synthesis and the oxidation after polymerization. The obtained results show that the PIs synthesized at different temperatures present quite similar thermogravimetric behavior and UV absorption spectra. Nevertheless, FTIR and XPS characterizations reveal significant differences in chemical composition and polymer structure depending on this polymerization temperature. At higher temperatures, indenyl coupling proceeds via 1,2 carbon atoms to obtain more compact and less defective polyindenes with higher yields. At lower temperatures, polymerization through 1,3 carbon atoms may also occur, leading to polymers with a larger number of defects and oxygen functionalities,

probably coming from ambient H₂O dissolved in CH₂Cl₂, and lower yields. The treatment with FeCl₃ caused the introduction of some oxygen functionalities in the compact PIn60 and PIn80 polymers, without significantly affecting their molecular structure and electrical conductivity. Finally, cyclic voltammetry demonstrates that, despite not electro-active, these partially oxidized polyindenes show enough electrical conductivity for different applications.

Key words: polyindene, oxidized polyindene, XPS, electrical conductivity, cyclic voltammetry

1. Introduction

The synthesis and characterization of conducting polymers has attracted considerable attention over the last decades. The main reason may be probably the wide range of potential applications proposed for these materials, mainly in optoelectronics and electrochemical devices, such as sensors, supercapacitors, batteries, etc.^[1,2] Because of that, various conductive polymers have been extensively studied in literature, highlighting polyanilines, poly(pyrrole)s, poly(thiophene)s, polyfluorenes, etc., so their molecular structure and physico-chemical and electrochemical properties, depending on the synthetic method and conditions, have been well established.^[3,4] However, these conducting polymers usually exhibit poor thermal and oxidative stability and are difficult to process.

By contrast, polyindenes (PIs) constitute a much less studied family of conducting polymers. The interest of PIs arises from the potential valorisation of indene, a by-product of the petrochemical industry, as a cheap raw material source for the preparation of valuable polymeric materials. Basically, these polymers are based on interconnected phenyl-cyclopentane fused rings, coming from indene, that horizontally arrange along the main chain.^[5] This structure provides PIs a planar conformation, high glass transition temperature (T_g)^[6,7] and interesting optical properties.^[5,7,8] Besides, the extended π -conjugation, coplanarity and the presence of polarons^[6,8-10] have been proposed to be responsible of the

electrical conductivity in this system, showing values ranging from $1.1 \cdot 10^{-5}$ to $7.9 \cdot 10^{-4}$ S/cm.^[8-10] Accordingly, PIns find potential application in areas such as solar energy systems, photoelectronics, electrochromic devices, etc. On the other hand, chemical modifications of PIns via sulfonation or hydrogenation have been studied to obtain polymers for proton-exchange membrane fuel cells (PEMFCs)^[11,12] and/or with interesting thermal properties,^[13] respectively. Furthermore, oxidized PIns were found interesting for a variety of applications,^[10] and PIns and their composites with inorganic particles have exhibited interesting electrorheological properties.^[14-16]

In spite of these interesting properties, PIns show lower conductivity than conventional conducting polymers, limited thermal stability, and too rigidity and brittleness that hamper their suitability and processability for some applications. Accordingly, various studies have demonstrated that these features of PIns can be improved by blending or forming copolymers with coumarone,^[17] vinyl monomers,^[18] methyldiene,^[19] pyrrole,^[20,21] styrenes,^[5,10] ethylene,^[10] polyoxomethylene,^[9] and others;^[7] or composites with Montmorillonite.^[6,16]

Various procedures to synthesize PIns can be found in literature, highlighting the electrochemical polymerization in CH_2Cl_2 at room temperature,^[10,20] and chemical oxidative polymerization using different acidic/oxidizing catalysts and conditions: (i) AlCl_3 in $\text{CH}_3\text{CH}_2\text{Cl}_2$,^[7,11,12] and cumyl methyl ether/ TiCl_4 ^[13] and $\text{CCl}_3\text{COOH}/\text{SnCl}_4$ in CH_2Cl_2 ,^[5] at low temperature (-20 to -65 °C); (ii) and FeCl_3 in CHCl_3 ^[6,9,14-16] or concentrated H_2SO_4 ^[8,21,22] at ambient temperature 15-25 °C. All these processes to obtain PIn are based on the cationic polymerization mechanism^[5,8-10,21,22] and were carried out under inert atmosphere and anhydrous conditions. A low-defective ideal planar structure was deduced for these PIns from their characterization with different techniques.^[5,8-10,21,22]

The use of inert and anhydrous conditions, low temperatures, and these cationic initiators, however, hinders and significantly increases the cost of PIns synthesized by these

procedures. Additionally, the separation of some of these catalysts from the polymer is not always possible and might entail environmental disposal problems. On the other hand, special environmental concerns may arise also from the utilization of concentrated H_2SO_4 as catalyst, which even has been reported to introduce $-\text{SO}_2$ groups in the polymer.^[8,21,22]

Interestingly, H^+ -exchanged montmorillonite, like Maghnite- H^+ (Mag- H^+), has been proposed as a non-toxic and cheaper acid catalyst to initiate cationic polymerizations of vinyl and heterocyclic monomers.^[23-26] Indeed, the synthesis of PIn by cationic polymerization of indene in CH_2Cl_2 with Mag- H^+ clay was previously reported.^[27] To simplify the procedure, CH_2Cl_2 was neither deaerated nor specifically dehydrated. Effects of the amount of Mag- H^+ clay, time and temperature on the polymerization were studied. Despite the advantages of this route to produce PIn, the molecular structure and polymerization mechanism of the obtained polymers was not analyzed, and their thermal, optical and electrical properties were not evaluated. Moreover, studies on the stability/reactivity and potential molecular-properties changes of PIn by chemical oxidation are lacking.

The present work covers the synthesis and detailed characterization of PIn obtained by Mag- H^+ -initiated cationic polymerization of indene at different temperatures (20-80°C). Particularly, the study presents completed and fully interpreted new experimental results on the chemical composition and molecular structure, as well as thermal, optical, electrical and electrochemical properties of the different PIn synthesized by this procedure. The influence of the polymerization temperature has been analyzed. For the characterization, thermogravimetry, UV and FTIR spectroscopies and conductivity measurements were carried out. Furthermore, to the knowledge of the authors, two powerful techniques, like XPS and cyclic voltammetry, have been used for the first time to characterize PIn. Finally, another novelty of the present work is the first study about the oxidative post-treatment of the PIn with FeCl_3 . The structure and properties of the obtained oxidized PIn derivatives (PInO) were also analysed by the same techniques.

2. Experimental

2.1. Materials

Natural bentonite was kindly supplied by Maghnia society of Algeria. Indene (99%, Aldrich) was distilled in vacuum before to use. Anhydrous FeCl_3 (98%, pure), dichloromethane (98% pure), ethanol (99% pure) and all the solvents were purchased from Aldrich and used as received.

2.2. Synthesis of polyindene (PIn) and oxidized polyindene (PInO)

2.2.1. Synthesis of polyindene (PIn)

Polymerizations were carried out in stirred flasks at different temperatures. In a typical synthesis, the catalyst (mineral clay) was dried in a muffle oven at 120 °C overnight and then transferred to a vacuum desiccator containing P_2O_5 . After cooling to room temperature under vacuum, the mineral was added to 2 g of indene in the presence of air, which was preliminarily kept in a magnetic stirred flask at the desired temperature, for example 20 °C. The resulting mixture was dissolved in dichloromethane (CH_2Cl_2). At the required time (6 hours), an aliquot of the reaction mixture was then taken and filtered to exclude any clay mineral. The polymer (PIn) was redissolved in CH_2Cl_2 and precipitated in ethanol for characterization. The same procedure was applied for the other polymerizations at 40, 60 and 80 °C. The as prepared polymers are referred to as *PInT*, being *T* the different reaction temperature.

The conversion yield of indene into polyindene was calculated from the initial mass of indene and the weight of the obtained polymer, which was obtained in the form of a white powder. The results of different yields as a function of the reaction temperature are given in Table 1.

Table 1: Effect the reaction temperature on the yield of different polyindenenes (PIn).

From Table 1 it is observed that the yield of PInS increases with increasing temperature. This effect was also observed by other authors. ^[5] This is assigned to the increase in the polymerization reaction rate with temperature, leading to a larger product formation during a fix reaction time. ^[23,24,27]

2.2.2. Synthesis of oxidized derivatives polyindene (PInO)

Four oxidized polyindenes (PInO) were prepared from the respective powdery polyindenes (PIn) synthesized at different temperatures. To do so, the oxidizing agent FeCl₃ was dissolved in 20 mL of chloroform and put in contact with the PIn with a FeCl₃:PIn = 1:1 weight ratio (0.150 g for each one).

The oxidation was carried at room temperature (15-20 °C) for 24 h. The resulting black oxidized products (PInO) were filtered and then washed several times with distilled water, subjected to vapour rotation to remove the solvent and dried in a vacuum oven at 80 °C for 24 h. The same procedure was applied for the oxidation of the different PInS and four different PInOs products were recovered with yields ranging between 60-80 %.

2.3. Characterization

Fourier transform infrared (FTIR) spectra were recorded on an ATI Mattson Genesis II FTIR TM spectrometer (400-4000 cm⁻¹) using the KBr pressed discs. Thermogravimetric analysis (TGA) of the polymers (PIn and PInO) was carried out in a TGA/SDTA851e/LF/1600 equipment (Mettler Toledo) by using samples of ca. 10 mg. For ultraviolet (UV) absorption spectroscopy, the polymers were dissolved in dichloromethane and analysed in a Jasco V-670 UV-vis-NIR spectrometer over the wavelength range of 190-400 nm. The XPS spectra were measured with a VG-Microtech Multilab electron spectrometer using non-monochromatized Mg K α (1253.6eV) from a twin anode source operated at 300 W (20 mA, 5 kV). The deconvolution of XPS spectra was done by least squares using asymmetric pseudo-Voigt functions (and constant profile shape factor of 0.3).

The electrical conductivity of the polymers, shaped into pellets, was measured with a Lucas Lab resistivity equipment with four probes in-line. The electrochemical behavior of the polymers was studied by cyclic voltammetry in a conventional 3-electrode cell. For the preparation of working electrodes, a given volume of polymer dispersion (1 mg/mL in CH₂Cl₂) was deposited and dried on the tip of a glassy carbon (GC) rod (3 mm diameter). A Pt wire was used as a counter electrode and commercial Ag/AgCl/Cl⁻ (3.0 M KCl) as reference electrode. The measurements were carried out at 50 mV/s in a N₂-deaerated 0.1 M HClO₄ aqueous solution by using a VSP potentiostat (from Bio-logic Science Instruments).

3. RESULTS AND DISCUSSIONS

3.1. Physico-chemical properties of powder polyindene (PIn)

3.1.1. Thermogravimetric (TG) analysis

The thermal behavior of the different PIns was followed in a thermobalance under inert atmosphere (Figure 1). For comparison purposes, the response of the clay catalyst is also depicted. As it can be observed, on the one hand, all the polymers undergone a quite-similar main decomposition process that accounts for the 98.2-99.7 % of the initial mass (Fig. 1A). Particularly, in all cases the polymers start to lose weight from ca. 270 °C and finish their decomposition at ca. 445 °C, reaching the maximum decomposition rate at 388-391 °C (Fig. 1B). This thermal behavior is similar to that observed for PIns synthesized by other procedures.^[6,8,10,11,20] The obtained total weight losses of close to 100 % indicate that practically the whole polymers decompose into gaseous products upon heating, leaving insignificant residues. In this sense, considering that the Mag-H⁺ used as catalyst only losses a 13.2 wt.% during a similar heating treatment (Fig. 1A), the observed 100 wt.% total losses confirm that the catalyst was effectively eliminated during the simple filtration step. On the other hand, a coupled decomposition process of low intensity (less than 3 %) can be discerned for the different polymers at lower temperatures (between 100-270 °C). This may be assigned

to the release of water molecules which is higher in the polymer prepared at lower temperatures.

Figure 1. Normalized (A) TG and DTG (B) curves of the PInS prepared at different temperatures. N₂ atmosphere (100 mL/min); heating rate = 10 °C/min.

The similar TG curves observed for the different polymers reflect they may be made of quite similar chemical bonds and/or structures. Nevertheless, there are some differences in their thermal behavior that can be mentioned. First, the pre-decomposition process at lower temperatures becomes more significant for the polymers prepared at lower temperatures (inset of Fig. 1A). Second, whereas this pre-decomposition is faster and totally coupled with the main process for the sample prepared at the lowest temperature (PIn20), it seems to be decelerated for the polymers synthesized at higher temperatures (inset of Fig. 1B). Specifically, this pre-decomposition is more defined for the sample prepared at 40 °C, and the thermal behaviors for PIn60 and PIn80 are almost identical. Third, the maximum rate and the end of decomposition for the PIn20 polymer appear slightly shifted towards lower temperatures compared to the samples prepared at higher ones. Hence, although minimal, the temperature for the polymer synthesis has a slight effect on their degradation temperatures.

3.1.2. UV spectroscopy

Ultraviolet (UV) analysis (in CHCl₃ medium) was carried out in the range 190-400 nm. As shown in Figure 2, all the polymers synthesized at different temperatures exhibit quite similar spectra, with two intense absorption bands around 223 and 270 nm. These spectra are more like those found by Brum et al. for PInS obtained with AlCl₃ catalyst at -20 °C [7]. The strongest band with maximum absorption at ca. 270 nm is characteristic of π - π^* absorption in indene;^[7,8,21] whereas the sharp band at 223 nm has been associated to the overlap of the π -conjugated bonds of indene-phenyl groups in the polymer backbone.^[7] Hence, this band supports the interconnection of indene monomers in the form of polymeric chains.

Figure 2. UV absorption spectra of PInS prepared at different temperatures.

Furthermore, a shoulder is observed above 280 nm in the spectra of the polymers. Shoulder-like features near 320 nm were observed by other authors ^[8,21] and were related to indanyl and dimer cation formation during PIn growing and/or the protonated state of PIn,^[28] species which are in line with the indene polymerization mechanism earlier proposed by different authors.^[5,8-10,21,22] On the other hand, Goel et al. attributed this broad absorption shoulder to the presence of carbonyl (C=O) groups, whose repulsion with hydrogens of adjacent phenyl rings in PIns might affect their chain conformation and, therefore, their absorption bands.^[8] Considering that this shoulder is much more marked in the case of PIn20 polymer, which presents a larger content of oxygen functional groups (see below FTIR and XPS characterization), it is then mainly attributed to the presence of these defects.

3.1.3. FTIR spectroscopy

Figure 3 shows the IR transmittance spectra of the polyindenes synthesized at different temperatures. The spectra were normalized for comparison and represented in a scale from 0 to -1. It is observed that, roughly, all the spectra display the same characteristic bands, indicating that all the samples possess similar functional groups.

Table 2 compiles the position and assignation ^[29] of the main bands observed in the spectra of Figure 3, stressing in bold those of higher relative intensity. These bands were also observed in other PIns reported in literature ^[6-11,14,20,22] and can be classified into 4 groups. First, the bands between 3020-3070 cm^{-1} and those at 717 and 748 cm^{-1} are assigned to the stretching and the out of plane deformation, respectively, of C-H bonds in aromatic structures, as those of benzene rings in indenyl units. Although less intense, the band at 1026 cm^{-1} may be due to in-plane bending of these aromatic C-H bonds. Second, the bands at 2846 and 2916 cm^{-1} are associated to C-H stretching in -CH₂- aliphatic bonds. These sp³ groups may come from the C=C bond in cyclopentene rings after coupling reactions (see below in the polymeric structures of scheme 1). Third, the three bands at 1458, 1585 and 1605 cm^{-1} are a group of features generally related with the aromatic and/or alkene-like conjugated C=C stretching. All

these bands agree with the molecular structure of polyindene proposed in literature [5,8-10,21,22] (see also the product 3 in the scheme 1).

Figure 3. FTIR transmittance spectra of the polyindenes prepared at different temperatures.

Finally, the fourth group is composed of different spectral features related with different functional groups. Thus, this group includes the broad asymmetric bands between 3000-3700 cm^{-1} , attributed to O-H stretching in alcohols, phenols, carboxylic acids or H_2O ; the band at 1713 cm^{-1} , due to the C=O stretching in carboxylic acids; and the bands at 1088 and 1207 cm^{-1} assigned to C-O stretching in primary/secondary alcohols and phenols, respectively. In addition, the various bands between 1330-1440 cm^{-1} may be associated to O-H and/or C-O bending, and that between 1250-1300 cm^{-1} to C-O stretching in carboxylic acids. The origin of these oxygen functional groups (carboxylic and alcohol groups) may be the oxidation of the monomer and/or the polymeric chain during the catalysed polymerization reaction (see later in the scheme 1). Given the fact the reaction takes place in CH_2Cl_2 , the oxygen atoms attached to the polymer may come from retained water molecules and/or surface hydroxyl groups on the clay catalyst [30] and/or atmospheric water molecules dissolved in exposed CH_2Cl_2 . Since all these functionalities were not expected in the proposed molecular structure of polyindene, they can be considered structural defects of the polymers. Moreover, the oxidation of the polymer as consequence of the air exposition cannot be discarded.

Table 2. Summary of wavenumber and assignation [29] of the main IR bands found for the polyindenes prepared at different temperatures (Fig. 3).

The intensity of these main bands was plotted as a function of the synthetic temperature. Figure 4A reveals that the relative intensities of the aromatic C-H stretching ($I_{C-H(Ar)st}$) and bending ($I_{C-H(Ar)b}$) bands and that of the methylene C-H stretching ($I_{C-H(CH_2)}$) generally increase with the temperature of polymerization (Figure 4A). On the other hand, the increase in temperature causes a decrease in the relative intensity of C=C

stretching bands ($I_{C=C}$), as well as those associated to oxygen functionalities ($I_{C-O}, I_{C=O}$). It is noteworthy to mention that even the polymers prepared at higher temperatures (PIn60 and PIn80) displayed the bands of oxygen functionalities. Respect to the band of O–H stretching, the sample prepared at 40° C shows the highest relative intensity (Fig. 3). This band contains not only the contribution of oxygen functionalities (alcohols and carboxylic acids), but also that of hydration, so it is not exclusively related to the polymer structure and, therefore, not proper for direct comparisons.

Figure 4. Effect of the synthetic temperature on the intensity of main IR bands (A), and on the ratio of some IR bands (B). Note : $I_{C-H(Ar)} = I_{C-H(Ar)st} + I_{C-H(Ar)b}$; $\sum I_{PIn} = I_{C-H(Ar)} + I_{C-H(CH_2)}$; $\sum I_{defects} = I_{C=C} + I_{C-O} + I_{C=O}$.

Apart from these individual trends, the intensity of these major bands was intercorrelated to obtain more meaningful information. Respect to the bands associated to $>C=C<$ species, an increase in the $I_{C-H(Ar)}/I_{C=C}$ ratio with the temperature is observed (black line in Fig. 4B). This suggests a relative decrease in substituted C=C bonds with temperature. On the other hand, concerning the formation of new bonds/species, the $I_{C-H(CH_2)}/(I_{C-O} + I_{C=O})$ ratio increases with temperature (blue line in Fig. 4B). This result seems to point out a progressive release of oxygen functionalities with an increase in alkyl connectivity. Interestingly, it can be observed (red line in Fig. 4B) that the ratio between the sum of band-intensities associated to a defect-free polyindene ($\sum I_{PIn}$), respect to the sum of those associated to defects in this structure ($\sum I_{defects}$), gradually increases with temperature. In other words, the proportion of defective features in the polyindenes decreases with the temperature of polymerization.

A brief discussion is necessary to interpret the obtained results. The relative increase in aromatic C-H bonds with temperature is assigned to the formation of a polyindene product with less substituted aromatic rings. On the other hand, the relative increase in alkyl -CH₂-

groups with temperature may be related to a favoured participation/destruction of C=C bonds (1 and 2 carbon atoms in cyclopentene) during monomer coupling in the polymerization reaction. These results suggest that at higher temperatures the reaction favours the formation of polymers with a molecular structure close to the previously proposed one (see the reaction pathway 3 and its product in the scheme 1). By contrast, at lower synthetic temperatures the proportion of oxygen functionalities in the obtained polymer increases. This finding seems to point out that under these conditions the participation of oxidative reactions during polymerization becomes more important (see the reaction pathway 1 and its product in the scheme 1). This could be explained by considering that (i) the kinetics of monomer coupling must be greatly enhanced at increasing temperatures, at least, in a greater extent than those of oxidative nature with the participation of H₂O; and/or (ii) higher temperatures could facilitate the release of water molecules and the oxidation of the polymer and/or avoid the formation of other structural defects in the polymeric chain.

Scheme 1. Proposed molecular structures and synthesis pathways for the polyindenes prepared at different temperatures.

Respect to the bands associated to C=C stretching, their increased relative intensity ($I_{C=C}$) for the polymers prepared at lower temperatures may be difficult to rationalize with the aforementioned polymerization mechanism (pathway 3 in the scheme 1). First, this mechanism predicts that one C=C bond is converted into two -CH₂- during monomer coupling, so one should expect a similar proportion of C=C bonds in the polymers prepared at different temperatures (i.e. the remaining three C=C bonds per benzene ring in the coupled monomer). Second, one might expect that an increased in aromatic C-H bonds (observed at higher temperatures) should be accompanied by an increased number of aromatic C=C bonds. Hence, to explain the obtained results we propose the occurrence of an alternative polymerization mechanism involving the participation of the 1 and 3 carbon atoms in cyclopentene (see the reaction pathway 2 and its product in the scheme 1). Again,

the slower kinetics for monomer coupling at lower temperatures may provide extra time to the indenyl cation intermediate to stabilize and react through the carbon atom in position 3. This different connectivity would break the linearity and would open the packed/compact molecular structure of the polyindene. Furthermore, compared to the proposed structure of polyindene, this *1-3* connectivity would enable the existence of an extra C=C bond that, on the one hand, would explain the increased relative intensity of C=C stretching in polymers obtained at lower temperatures; and, on the other hand, would result in a planar arrangement of monomers and, thus, a less compact structure.

All these proposed explanations and mechanisms are in line with the observed gradual change (increasing $\sum I_{PIN}/\sum I_{defects}$ ratio) from more to less defective polyindene structure with temperature. Furthermore, the molecular structures proposed for the polymers synthesized at lower temperatures, with *1,3* connectivity and a larger proportion of defects (see the polyindene product 1 in the scheme 1), would reasonably hinder the enlargement (chain growth) of the polymer, what agrees with the lower polymerization yields obtained at lower temperatures (Table 1).

3.1.4. XPS spectroscopy

XPS is a powerful surface analytical technique and provides valuable quantitative and chemical state information of the surface of the polyindenes synthesized at different temperatures. The atomic and weight composition of the different polymers is summarized in Table 3. The obtained results show that, in all cases, the obtained products are mainly formed of carbon atoms (≥ 89 at. %), although some oxygen was found. The maximum oxygen content, ca. 11 at%, was found for the product obtained at the lowest temperature (20 °C). This oxygen content remarkably decreased down to 1-3 at % for the polymers prepared at higher temperatures (40-80 °C). These results seem to agree FTIR analysis.

Table 3. XPS atomic and weight surface composition of the different polymers.

The analysis and deconvolution of the C(1s) and O(1s) core-level spectra provided interesting qualitative information of the different polymers. To the knowledge of the authors, XPS characterization of polyindene has not been reported in the literature. However, the reported data of other conductive polymers, like polyaniline and polypyrrole, may be useful for comparative purposes.

The C(1s) spectrum of the different materials (see two examples in Figure 5A,B) shows a main peak centred at ca. 284.5 eV which has been commonly assigned to carbon-carbon bonds.^[31-33] This peak, however, has been reported to include the contribution of sp^3 (at ca. 284.6 ± 0.1 eV) and sp^2 (at ca. 284.2 ± 0.1 eV) hybridizations.^[31-33] Hence, and in line with the structure proposed for polyindene (scheme 1), the C (1s) spectra of the different PIn samples were deconvoluted considering these sp^3 and sp^2 contributions (Fig. 5A-B). Interestingly, as it can be observed in Fig. 5C, the relative proportion of sp^3 hybridization was found to increase with the polymerization temperature. Given the fact that, compared to the indene monomer, the significance of sp^3 hybridizations may increase with the degree of polymerization (see scheme 1), the increase in sp^3/sp^2 ratio suggests that an increase in the reaction temperature may promote the polymerization reaction. This would agree with the increasing yield at increasing reaction temperatures (Table 1), as well as the increase in C-H (CH_2) and decrease in C=C bonds for the polymers synthesized at higher temperatures found by FTIR (Figure 4).

Figure 5. C(1s) XPS spectra of different polyindenes (PIn20, PIn80 and PInO80) and the effect of the reaction temperature on the relative contribution of sp^3 to sp^2 hybridizations.

A second contribution appears at 285.9 ± 0.1 eV in the C(1s) spectra of the different polymers. The relative contribution of this peak to the C(1s) spectrum is maximum for the samples prepared at lower temperatures (ca. 9 at% of C(1s) signal for PIn20 and PIn40), and then it seems to decrease with the temperature of synthesis down to 5 and 3 at% for samples obtained at 60 and 80 °C, respectively. This has been attributed to aromatic carbon bound to

oxygen-containing -C-O structures in polymeric materials [32,33] and agrees with the contribution at 532.0 eV in the deconvoluted O(1s) spectra (see below an example in Fig. 8).

At higher binding energies in the C(1s) spectrum, the sample prepared at the lowest temperature (PIn20) shows another contribution (of ca. 4 at%) at 288.8 eV (Fig. 4a). This has been related to C=O bonds in carboxylic groups (O-C=O) [31-33], coinciding with the contribution at ca. 533.4 eV observed in the O(1s) spectrum of this sample (see examples in Fig. 8). For the samples prepared at higher temperatures, the O-C=O contribution in the C(1s) spectrum is not observed, and that in the O(1s) signal seems to appear with low intensity and greatly overlapped. This suggests a more severe oxidation of the monomer and/or polymeric chain when obtained at lower temperature, what agrees with the results of FTIR characterization (see also the scheme 1).

Samples prepared at higher temperatures (40-80 °C) exhibit a new band at 291.1 ± 0.2 eV, whose relative contribution seems to increase with temperature from 2.9 to 3.2 %. This contribution has been generally assigned to $\pi-\pi^*$ (HOMO-LUMO) transitions, involving a characteristic shake-up line (satellite peak), for carbon atoms in aromatic and/or conjugated compounds.^[31,32,34] In this sense, the observance of this band must be related to the formation of a polymer product with a larger amount or proportion of aromatic units and/or a longer conjugated system.

The obtained XPS results support that higher reaction temperatures favour the synthesis of polyindenes with higher yields, a lower number of defects and/or a larger proportion of aromatic/conjugated structures.

3.2. Physico-chemical properties of oxidized polyindenes (PInOs)

Because of their less defective structure, the study on the oxidation of polyindenes was focused only on the two polymers oxidized at the highest temperatures, i.e. PIn60 and PIn80.

3.2.1. Thermogravimetric (TG) analysis of oxidized polyindenes

Figure 6 compares the normalized TG curves of PIn60 and PIn80 samples before and after oxidation with FeCl₃. For both samples, the oxidation produces similar effects. First, the extent of the main decomposition process is reduced from close to 100 % to 84 and 81 % for the PInO60 and PInO80 samples, respectively. Second, the main decomposition process is shifted 15 °C and 10 °C (for the maximum rate) towards lower temperatures for these samples, respectively. Third, the coupled pre-decomposition process below 300 °C is significantly enhanced in both cases.

The enhanced pre-decomposition process, associated with the release of water molecules, points out that the treatment with FeCl₃. The presence of a higher proportion of this water, showing less thermal stability, may explain the shift of the process towards lower temperatures. Nevertheless, the ca. 20 wt.% residue remaining after heating the oxidized samples suggests that they might suffer from cross-linking or any oxidative reaction, during FeCl₃ treatment or TG analysis, leading to the stabilization of parts of the polymer.

Figure 6. Normalized TG curves of PIn60 (A) and PIn80 (B) samples before and after oxidation. Inlet: DTG curves of the samples.

3.2.2. FTIR spectroscopy of oxidized polyindenes

The treatment with FeCl₃ produced similar effects on the FTIR spectra of PIn60 and PIn80 samples. Figures 7 compares, the normalized FTIR spectra of the PIn60 and PIn80 before and after FeCl₃ treatment. Overall, it can be inferred that this treatment produced similar effects on the FTIR spectra of both samples. As it can be observed in Fig. 7B, the PIn60 and PInO60 polymers present quite similar spectra. Nevertheless, some changes can be stressed. After the treatment with FeCl₃, (i) the relative intensity of the aromatic C-H stretching bands (3015-3070 cm⁻¹) slightly decreases; (ii) the bands at 1601, 1586 and 1456 cm⁻¹ related to C=C stretching become more intense; (iii) and those associated with oxygen functional groups; i.e. the C=O stretching (1713 cm⁻¹) in carboxylic acids, and the O-H bending (1440 cm⁻¹) and the C-O stretching (1154 and 1088 cm⁻¹) in alcohols slightly

increase. Furthermore, (iv) other oxygen-related vibrations, such as the O-H stretching at 3300-3400 cm^{-1} and the C=O stretching at 1650 cm^{-1} appear. All these features have been associated with the presence of defects as consequence of the oxidation in the molecular structure of polyindene (see section 3.1.2).

These results seem to indicate that the FeCl_3 treatment introduces in the less defective polyindenes (those synthesized at higher temperatures) the same type of defects that have been observed in the polymers obtained at lower temperatures. However, the changes on the aromatic C-H stretching and bending bands are not dramatic, suggesting that the substitution of the benzene rings may be not significant. Interestingly, the increase in the relative intensity of the bands at 2920 and 2849 cm^{-1} ; associated to the C-H stretching in -CH-/CH₂- connections, may be due to the transformation of C=C bonds into sp^3 species, although a slight net increase in the intensity of C=C band is observed. These C=C bonds could be those formed by 1,3 coupling during polymerization (see the mechanism 1 and 2 in the scheme 1). In addition, this transformation could be accompanied by the incorporation of some alcohol groups. Hence, the structure of the PInO60 must be like that of PIn60 with a lower proportion of interconnecting C=C bonds and some extra oxygen functionalities.

Figure 7. FT-IR spectra of PIns prepared at 60 and 80 °C and their respective oxidized products.

Concerning the PIn80 polymer, Fig. 7B shows that the FeCl_3 treatment causes quite similar or even less changes. The main differences in this case are a larger decrease in the intensity of the C-H (Ar) stretching, which may be associated to the introduction of phenol groups (at 1205 cm^{-1}), and the reduction in the relative intensity of the C-H stretching in -CH-/CH₂- connections, which may be related to the incorporation of alcohol (O-H stretching at 3300-3400 cm^{-1}) and ketone-like (C=O stretching at 1650 cm^{-1}) groups. These results infer that the molecular structure of the polymer PInO80 must be that of the polyindene (see the product 3 in the scheme 1) with additional oxygen functionalities.

3.2.3. XPS analysis of oxidized polyindenes

The oxidized derivatives of PIn were analysed by XPS. As it can be seen in Table 3, the oxidation treatment of PIn60 and PIn80 with FeCl₃ increased the surface oxygen content between 2.5-3.0 times up to 7-9 at.%. This increment in oxygen functional groups is in line with the enhanced weight-losses of the pre-decomposition processes in the TG curves of the treated samples (Fig. 6).

Respect to the type of oxygen functionalities, Figure 5D shows the deconvoluted C(1s) spectra of the PIn80 polymer (as example) before and after FeCl₃ treatment. The assignment of the different contributions was described in section 3.1.3. On the other hand, Figure 8 presents the deconvoluted O(1s) spectra of the pristine and oxidized PIn60 and PIn80 samples. In all cases, the O(1s) spectra were fitted to four contributions, including the presence of carboxyl (O–C=O, at 531.5 ± 0.2 eV) and ketone-like (C=O, at 532.2 ± 0.1 eV) double bonds; and the carboxyl (O–C=O, at 533.1 ± 0.1 eV) and alcohol/phenol (C–OH, at 534.0 ± 0.2 eV) single bonds [31,34].

As it can be observed in both figures, the changes in the C1s and O1s core-level spectra of PIn60 and PIn80 were quite similar. Thus, both PInO60 and PInO80 experienced a relative increase in C=O bonds in the C1s spectrum (see the example of PInO80 in Figure 5D), whereas the O1s spectra of both oxidized samples showed a relative increase in the contributions at ca. 532.2 eV assigned to ketone-like groups (Figure 8). Moreover, an increase in the relative intensity of carboxylic C=O at 531.5 eV is also observed for PIn60. These results agree with the changes observed on FTIR spectra (Figure 7).

Figure 8. O(1s) XPS spectra of the polyindenes PIn60 and PIn80 before and after treatment with FeCl₃.

Another interesting result is that, despite the incorporation of oxygen functionalities and/or their associated defects, the π - π^* band (at ca. 291.1 ± 0.2 eV) also appears in the C(1s)

spectra of the oxidized products (see the example of Fig. 5D). This indicates that the aromaticity and/or the conjugated system is well conserved after the treatment with FeCl_3 .

3.3. Electrical conductivity and electrochemical properties

3.3.1. Electrical conductivity of polyindene and oxidized derivatives

Table 4 collects the electrical conductivity of PIn40 and oxidized polyindenes PInO60 and PInO80. As it can be observed, the conductivity of the PIn40 sample obtained by Mag-H⁺-catalyzed polymerization is in the order of the higher values found for other pure PIns synthesized by other methods [8,10]. Despite their different molecular structure, however, the PIns obtained at the other temperatures showed quite similar conductivities ranging between $5.0\text{-}9.0 \times 10^{-4}$ S/cm, without a clear effect of the polymerization temperature.

Table 4: Electrical conductivity of different polymers (average of 5 measurements)

This electrical conductivity has been attributed to de-localization of π electrons in the π -conjugated system of PIn chains.^[6,8-10] From Gouy scale magnetic susceptibility measurements, some authors found that the conducting mechanism in PIns has a polaron nature.^[9,10] Hence, the presence of polarons may explain the conductivity of PIns, while the high planarity in their structure may lead to easier charge transport. In this sense, the UV bands at 223 nm observed for the studied PIns (Fig. 2), related to overlapping of π systems of phenyl rings, may justify the conductivity of these materials (Table 4); and the quite similar UV spectra of the PIns prepared at different temperatures agree with their similar conductivities. Besides, the presence of defects, as evidenced by different characterization techniques, could promote the formation and transport of charges and polaronic structures along the polymeric chains.

Interestingly, other authors reported significantly lower conductivities (in the order of $10^{-5}\text{-}10^{-6}$ S/cm) for PIns synthesized by using FeCl_3 as oxidant.^[6,9] Although no explanations have been proposed to now, this finding suggests that the oxidation or over-oxidation of the PIns could be detrimental for their conductivity. As shown in Table 4, the conductivity values

found for the post-oxidized polymers (PInOs) are higher or in the order of non-oxidized PInS. This result seems to indicate that after polymerization, the PInS are stable towards this kind of oxidation, at least to keep their original electrical conductivity. The non-significant structural changes after FeCl₃ treatment observed by FTIR characterization seem to support this stability of the PInS studied in this work.

Finally, the conductivities obtained for the different polymers deserve some further discussion. The dimensions of the polymeric chains may affect in the conductivity. Thus, the oxidized polyindenes synthesized at higher temperature (PInO80), whose polymerization proceeds more rapidly, are formed of polymeric chains of lower molecular weight,^[27] what could explain its lower conductivity compared to PInO60.

3.3.2. Electrochemical properties of polyindene and oxidized derivatives

The polyindenes were characterized by cyclic voltammetry in acid medium. To the knowledge of the authors, no voltammetric characterization of polyindenes can be found in the literature. Figure 9 compares the voltammetric response of a bare glassy carbon (GC) electrode with that of the GC supporting different amounts of PInO80 selected as example. It can be observed in the figure that the deposition of the polymer slightly reduced the currents (and enclosed area) of the voltammogram of the GC. Moreover, the current decrease augmented slightly with the amount of deposited polymer. However, the shape of the voltammogram was not affected. Interestingly, no tilt of the voltammogram, even at high scan rates 50-200 mV/s, was observed after depositing the polymer.

Figure 9. Steady-state cyclic voltammograms of a glassy carbon electrode before and after deposition of different amounts of the PInO80 sample. Inlet: photo of the tip of the GC bar with a deposit of 4 µg of PInO80 after electrochemical analysis.

A tilt of the voltammogram is generally associated to an increased in the electrical resistance of the electrode surface, so the obtained results agree with the conductive nature of the polymer. Nevertheless, the observed decreases in voltammetric currents/charges are

attributed to the lower conductivity and/or specific capacitance of the supported polymer, compare to that of GC.^[35,36] On the other hand, the similar shape of the voltammograms, without any new electrochemically-induced redox process, suggests that the polymer is not electroactive.

4. CONCLUSION

In this study, polyindenes have been synthesized at different temperatures by using a cheap Maghnite-H⁺ catalyst and simple route at ambient conditions. Moreover, oxidized polyindenes were derived by FeCl₃ treatment after polymerization. Characterization by FTIR and XPS revealed differences in chemical composition and molecular structure of the polymers obtained at different polymerization temperature. At higher temperatures, polymerization mainly proceeds via cyclopentene 1 and 2 carbon atoms, leading to low-defective polymers with a molecular structure closer to that predicted for polyindene; whereas at lower temperatures the proportion of oxygen functionalities in the polymer increases and 1-3 coupling of monomers also occurs, obtaining less linear polymeric chains. These differences are attributed to the participation of existing water in oxidative reactions during indene polymerization, and the distinct effect of temperature on the reaction kinetics of both oxidation and polymerization concurrent reactions. However, the obtained results indicate that, overall, the different polymers show quite similar thermal, optical and conductive behavior, independently of the synthetic temperature.

The analysis of the polymers after treatment with FeCl₃ reveals an increased in their oxygen content (oxidation), but the polymeric structures do not seem to be significantly affected and their electrical conductivity is greatly kept. These facts reflect the good chemical stability of these PIns. Moreover, the voltammetric characterization confirms the conductive nature of these polymers, supporting their potential interest for different electrical and electrochemical applications.

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