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# New results on the polymerisation of the itaconic acid in aqueous medium

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## Summary

Itaconic acid has been polymerised in aqueous medium using potassium persulphate as initiator. An important dependence on the polymer yield with the initial pH of the reaction medium is observed. Polymers obtained on this work showed to be mainly atactic, with around 1.14 of polydispersity and molecular weight around 5 x $10^5$ g/mol. All the polymers synthesized were characterized by FTIR, $^1$H-NMR, $^{13}$C-NMR, gpc, thermogravimetry and acid number. Analysis of these materials seem to indicate a decrease of acidity related to the lost of one carboxylic group from the itaconic acid residue, probably due to intramolecular interactions when the monomer is incorporated into the polymer growing chain.

## Introduction

Literature on the homopolymerisation of itaconic acid (IA) is limited **[1-5]** and the majority of studies have been dedicated to the copolymerisation of IA with different monomers **[6-15]** which is associated with:

a) improvement on the final properties of the polymers synthesized (better adhesive properties and swelling ability in water) **[10]**.
b) difficulties found during homopolymerisation of IA made researchers in the fifties believe that it was a non-polymerisable monomer **[2]**.

On the other hand, in recent years considerable attention has been paid in the search for materials that may mimic and be recognised by nature such as the mono **[11-13]** and diitaconate derivatives of IA **[14-18]**. It is important to remember that this acid is obtained from fermentation of carbohydrates. However, studies on the homopolimerisation of IA are still scarce. Due to the potential applications of polymers from IA, in the present study, we report the successful homopolimerisation of IA in aqueous medium by using potassium persulphate as initiator.

## Experimental

*Chemicals:* Itaconic acid (Sigma) was used without further purification and characterized by FTIR and $^1$H-NMR. All aqueous solutions were freshly prepared using water purified by a Millipore MilliQ$^{TM}$ deionising system. Potassium persulphate (PPS, Baker 99,4%), acetone (ACS 99,5%), sodium nitrate (Merck 99%), acetic acid (AA, Riedel de Haen 99,8%), potassium phthalate (Riedel de Haen 99.5%) and all chemicals were used without previous purification.

*Characterization:* Thermogravimetric analysis were performed using a TGA-7 Perkin-Elmer Thermobalance, IR spectra using a System 2000 Perkin-Elmer FTIR spectrophotometer and NMR spectra on DRX Bruker 300 MHz spectrophotometer. Potentiometric titrations and pH measurements were performed using 691 Metrohm pH-meter, conductimetric measurements were performed using 8033 Hanna Instrument conductimeter. GPC was performed using Perkin-Elmer HPLC with L-7110; ionic SB 806 Shodex OH Pak separation columns were used in series. Poly(acrylamide) standards in $NaNO_2$ aqueous solutions were used.

*Synthesis:* Deionised water (10 mL) was heated until boiling and left to reach ambient temperature with continuous stirring and under nitrogen bubbling. Itaconic acid (IA) (0.023 mol) and PSP ($2.22x10^{-4}$ mol) was added and the solution pH determined ($pH_i$). KOH was employed to adjust pH; the system was sealed and placed in a thermostatic bath at 60 $^0$C with continuous stirring during 48 h. A heterogeneous mixture was initially obtained due to an incomplete IA dissolving that turn to transparent after 5 minutes (samples at pH 2 and 2.4). Samples at pH=3 became cloudy during almost all the polymerisation process and then turn to pale yellow. After the polymerisation reaction time was over, the reactors were left to cool down to room temperature under continuous stirring (30 min). pH was measured ($pH_f$) and polymers were separated by precipitation in cool acetone. This sample was then dry and dissolved in the lowest possible amount of water. The resulting solution was filtered through a HV Millipore system (0.45 μm pore) and stored as solution. A hard vitreous but fragile material is obtained after removing solvent. Table 1 shows the yields for the polymers synthesized in this work.

Table 1. Average results of IA polymerisation in aqueous medium. T = 50°C

| Sample | IA | | pH | | time | Yield | | Mn | Mw | D |
|---|---|---|---|---|---|---|---|---|---|---|
| | (g) | (mmol) | Initial | Final | (h) | (g) | (%) | $x10^{-3}$ | $x10^3$ | |
| PIA-A | 3.0 | 23 | 2.0 | 1.9 | 48 | 1.4882 | 49 | 544 | 621 | 1.14 |
| PIA-B | 3.0 | 23 | 2.4 | 2.3 | 48 | 0.5233 | 17 | - | - | - |
| PIA-C | 3.0 | 23 | 3.0 | 2.4 | 48 | 0.5870 | 19 | - | - | - |
| PIA-D | 3.0 | 23 | 2.1 (*) | 1.7 | 48 | 0.3883 | 13 | 497 | 557 | 1.12 |

(*) 200 μl de acetic acid added

## Discussion

It is important to emphasize, under the experimental conditions employed in this work, that polymerisation of IA is strongly affected by the neutralization degree of the carboxylic group in the monomer and by the presence of other species in bulk of reaction medium, i.e. acetic acid. It has been observed a substantial decrease in the polymer yields when monomer is neutralized with KOH (table 1). This result may imply a minor reactivity of the carboxylated groups, which disagree with studies mentioned by Sandler and Karo **[5]** (i.e. Nagay reports no effect in the polymerisation rate constant to pH of 2.3-3.8 **[3]**). A possible explanation may consider that reaction of the anionic monomer with the growing chains are hindered by the bigger size of these species resulting in a decreasing of the reaction rate and consequently, in the yield. This result agrees with studies reported more recently **[6,19]**.

On the other hand, the use of an external acid in the reaction medium, like acetic acid, trend to decrease drastically the yield of the reaction (table 1, sample PAI-D). We believe that this result could be attributed to some kind of interaction between this(which acid polymer or acetic) acid and the initiator or propagating species.

Figure 1 show the transmission FTIR spectra obtained for (a) PIA-A film (from an aqueous solution by solvent evaporation to 50 °C) (b) IA in KBr pellet and (c) PIA-A in KBr pellet. Analysis of these spectra shows significant broadening for most of the characteristic bands obtained for PIA-A when compares with IA spectrum. Absence of the C=C stretching signal in fig 1a and 1c indicate that the polymerisation process has been carried out through the double bond of the monomer. The most intense band was observed at 1731 $cm^{-1}$; this has been assigned to C=O stretching and confirm the presence of carboxylic groups in the polymer. In addition, a small signal at 1852 $cm^{-1}$, better observed in the spectrum 1c, confirm the presence of some anhydride groups in the polymer backbone.

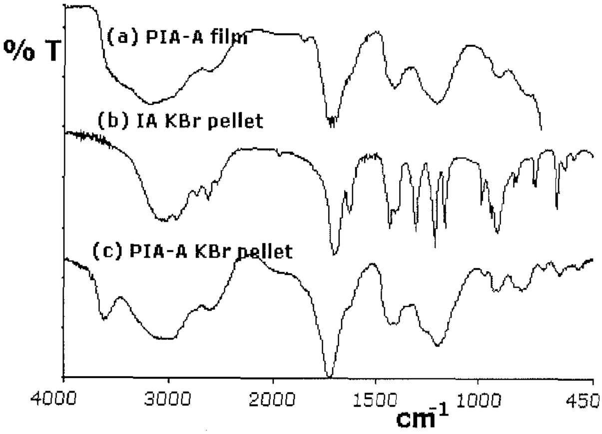


Fig. 1. FTIR spectra for (a) PIA-A film (b) itaconic acid in KBr pellet and (c) PIA-A in KBr pellet.

The signal at around 3450 $cm^{-1}$ is assigned to the free hydroxyl groups. The band around 3700 $cm^{-1}$ corresponds to water associated to the polymer, which agrees with the TGA studies (around 13 % lost weight) and can be clearly observed when the FTIR is made of KBr pellet (fig. 1c) but decreases when the spectrum is obtained from a film (fig. 1a). There was one other peak around 2610 $cm^{-1}$, which could be assigned to intramolecular hydrogen bonding between carboxylic acid groups. This signal does not change when the FTIR is obtained in KBr or film. Stretching and bending bands for methylene group are also observed.

Figure 2 shows amplified regions in $^{13}$C-RMN spectrum for PIA-A. Fig. 2 (a) shows region for type (a) and type (b) carboxylic carbons (structure I). Fig. 2 (b) shows methylenic and quaternary carbons. Signal assignments are summarized in table 2.

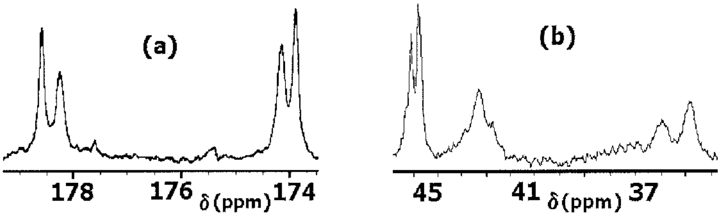
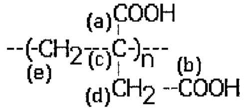


Fig. 2. PIA-A $^{13}$C-RMN spectrum amplified to (a) carboxylic region and (b) methylenic and quaternary carbons. Solvent: $D_2O$.



$$\text{--}(-\underset{(e)}{CH_2}-\underset{(d)CH_2-\overset{(b)}{COOH}}{\overset{(a)COOH}{\underset{(c)}{C}}}-)_n\text{--}$$

Structure I

Two signals corresponding to methylenic carbons (e) are located at 36 ppm ($-CH_2-$ between isotactic substituents) and 34.9 ppm ($-CH_2-$ between syndiotactic substituents). Signals at 47.1 and 46.8 ppm correspond to quaternary carbons having isotactic and syndiotactic configurations respectively. A not well-defined broad band is observed at 43.3 ppm, which corresponds to pendant methylene carbons.

Table 2. Signal assignment to the $^{13}$C-RMN spectrum for PIA-A.

| δ (ppm) | Assignments |
|---|---|
| 178.6 | rr triad COOH (a) |
| 178.25 | mr triad COOH (a) |
| 177.6 | mm triad COOH (a) |
| 175.4 | mm triad COOH (b) |
| 174.2 | mr triad COOH (b) |
| 173.8 | rr triad COOH (b) |
| 47.1 | quaternary carbon in the backbone chain with isotactic configuration (e) |
| 46.8 | quaternary carbon in the backbone chain with syndiotactic configuration (e) |
| 43.3 | $-CH_2-$ in the pendant groups (d) |
| 36 | $-CH_2-$ in the backbone chain between two isotactic substituents (c ) |
| 34.9 | $-CH_2-$ in the backbone chain between two syndiotactic substituents (c ) |

An estimate of the average length can be obtained to the different tacticity sequences when relative abundance of carboxylic carbons (a) and (b) was considered. Analysis of data from (a) carboxylic carbons allows determination of meso length sequences ($n_m$) average number by **[20]:**

$$\tilde{n}_m = (mm + 0.5mr)/0.5mr = (0.0811 + 0.5x0.4627)/0.5x0.4627 = 1.35$$

racemic length sequences ($n_r$) average number was obtained by:

$$\tilde{n}_r = (rr + 0.5mr)/0.5mr = (0.5402 + 0.5x0.3699)/0.5x0.3699 = 2.97$$

finally, polymer length sequences (n) average number was obtained by:

$$\tilde{n} = 1/(rr + 0.5mr) = 1/(05402 + 0.5x0.3699) = 1.45$$

These results indicate the presence of an atactic polymer, which possess longer syndiotactic sequences rather than isotactic sequences. However, presence of very short isotactic sequences avoids the growth of significant syndiotactic blocks. The considerations above are confirmed by $^1$H-RMN spectroscopy. Figure 3 shows the $^1$H-NMR for polymer PIA-A. Peaks at 2.8 and 2.7 ppm can be assigned to methylene protons from the main backbone located between quaternary carbons with isotactic and syndiotactic segments, respectively. This assignment is based on the intensities of both $^1$H-NMR signals and $^{13}$C-NMR results. In the case of pendant methylene protons, assignment is difficult mainly due to signals overlapping, but 2-D NMR analysis confirms the previous assignment of this protons.

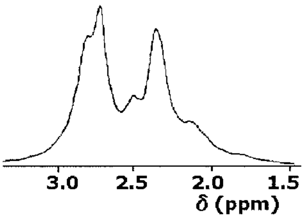


Fig. 3. $^1$H-RMN spectrum for PIA-A in $D_2O$.

Experimental acid number (AN) measurements from the different polymers synthesized show to be approximately half of the theoretical calculated value (table 3). Theoretical calculations were done assuming that acidity constants ($K_a$) of the acid groups from repetitive unit are very close to those in the free IA. The amount of water in the polymer was also considered to correct the measured AN values.

Table 3. Values obtained during AN determination of the PIA.

| Sample | Expected AN (mg KOH/sample weight) | Measured AN (mg KOH/sample weight) | Corrected AN (mg KOH/sample weight) |
|---|---|---|---|
| PAI-A | ~ 863 | 387 | 440 |
| PAI-C | ~ 863 | 322 | 365 |
| PAI-D | ~ 863 | 387 | 440 |

These results may be explained assuming that polymerisation process is leading to an important decrease in the acid dissociation constant ($K_{a2}$) when the monomer becomes part of the polymer backbone, turning the carboxylic acid group less acidic and blocking determination by titration. However, acid dissociation constant for methyl succinic acid, best structural mimic of the repetitive unit proposed for PIA, are high enough to be analytically determinate by titration **[21]**. Thus, changes related to transformation of the unsaturated part of the monomer during polymerization do not appear enough to explain AN results. A more reasonable explanation may be attributed to:

a) secondary structures in the polymer chains provide a hindering shield on the type A carboxylic acid group that inhibit (or prevent) titration under the experimental conditions.
b) presence of negative charges on the chain polymer, resulting from the first ionisation, becomes unfavourable (due to high charge density of the polymer) the presence of an additional close negative charge.
c) integrity of methyl succinic unit in the monomer is no longer preserved. Type (b) carboxylic acid group is able for titration but the other may be transformed in cyclic anhydrides or lactones or acetals or hemiacetals, through intramolecular reactions. However, as it has been discussed before, spectroscopic analysis indicates that these types of cyclic structures should not be present in a considerable extent.

Figure 4 shows the thermal responses (DTG) of polymers studied in this work at a heating rate of 10°C/min. All curves show the well-known low thermal stability of PIA. TGA thermograms show a continuous decreasing of the baseline as the temperature is raised. All the studied polymers exhibit four degradative processes between 30 °C and 480 °C. A peak at around 55-60 °C can be observed and corresponds to evaporation of water retained after synthesis or adsorbed from the environment. PIA-A presents higher water contents (around 13%) and higher ability to retain water when is compared to others synthesized polymers (final temperature around 130 °C compare to 105 °C for PIA-B/C). We believe that this behaviour is due to the existence of more free carboxylic groups in PIA-A, which are able to interact through strong hydrogen bonding with water, as was also observed by the FTIR analysis discussed before. Polymers synthesized to higher initial pH show minor water content and release it to lowest temperatures.

A second large peak between 130-260 °C is associated to anhydride formation and $H_2O$ evolved. Again, PIA-A shows higher degradation stability as can be observed from fig. 4 where the second degrading process is shifted around 30 °C from PIA/B. This behaviour is also associated to strong hydrogen bonding in this polymer.

The third degradative process may be attributed to decarboxylation of the previously formed anhydride groups. This behaviour has been reported for poly(monoalkyl-itaconates) **[11,13]** and seems also to involve reaction with carboxylic groups. Shift to higher temperatures observed for PIA-A may be attributed to the stability of the anhydride groups in this material. Probably, a series of reactions may be taking place between different

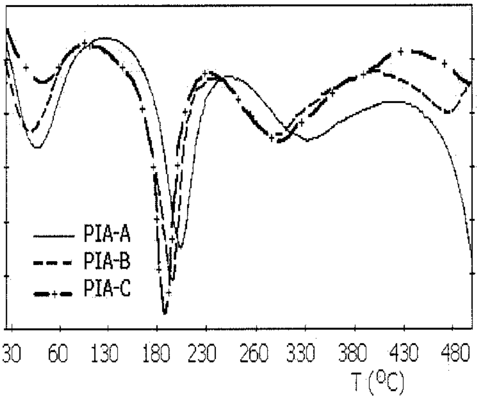


Fig. 4. DTGA curve for samples of PIA.

types of carboxylic groups existing in the polymer backbone, which could be associated to CO formation and decarboxylation. The presence of these chemical structures coming from the breaking off the main polymer backbone, may give rise to the fourth degradation process occurring at temperatures over 450 C.

## Conclusions.

This study provides relevant and important data to demonstrate that polymerization of IA in aqueous systems is highly dependant on the pH of the reaction medium, as will ionisable vinyl monomers. It is important to emphasize that this study provides experimental conditions to produce homopolymers of poly(itaconic acid) with high molecular weight, which has been confirm by GPC. Extreme control to remove oxygen from solutions employed seem to be an important fact to ensure polymerization with high molecular weight. The present result indicates that polymerization yield is strongly affected by initial pH of the solutions, reaching higher yields when not neutralized solution is used or in the absence of acetic acid. Polymers obtained from not neutralized solutions showed a relatively better ability to retain water but a lower capability to be expelled.

Analysis of the polymers synthesized show to possess mainly short syndiotactic segments in the polymer backbone, but we have to recognize that spectroscopic analysis regarding the integrity of carboxylic groups after polymerisation are not conclusive. On the other hand, TGA analysis clearly shows the low thermal stability of these polymers. Polymers synthesized from partially neutralized solutions show to possess lowest thermal stability.

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