Application of a New pH-metric Method to the Kinetic Study of Copolymerization of Polysaccharides Fucan N1 with PMMA in Presence of Cerium Ce^{+4}

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Abstract

The copolymerization of a Poly-Acrylic PMMA with polysaccharide, Fucan N1 and Dextran T70,in presence of a ceric salt used as initiator in acidic medium,was carried out under the following conditions: Fucan N1=0,5 g; $[CAN] = 3,6.10^{-3} M$, $[HNO_3] = 0,2 M$; temperature =40°C with a relative ratio between the initiator and the monomer, initiator/monomer =1/10. Besides a pH study of the reaction medium, an infrared spectroscopy (IR) proved the appropriatness of these best conditions of synthesis, and this by showing the presence of a characteristic peak of the carbonyl grouping situated at 1733cm^{-1} for the copolymer Fucan PMMA in respect to the individual PMMA spectra and Fucan N1. In addition, a ^{13}C NMR study has been conducted on the copolymer.

A viscosimetry study of two Fucan fractions was performed in aqueous medium (H$_2$0), and also of the obtained copolymer in DMSO.

An outcome of this work allows for us the suggestion of a plausible reaction mechanism, of which the copolymerization rate -Rp- is first order dependant to the monomer concentration, and to the square –concentration of both the initiator and the polysaccharide.

Keywords: Poly-acrylic, Copolymerization, Polysaccharide with ceric initiator

1. Introduction

The essential aim of this work is to apply the pH-metric measuring method to the study of the PMMA copolymerization with polysaccharides Fucan N1 and Dextran T70 (Fucan N1 is a sulfated polysaccharide extracted from a brown seaweed of the Ascopohyllum nodosum kind), in presence of ceric ions ce^{4+} in nitric acidic medium pH=1, at a temperature 4OC° during 40mn, under argon atmosphere (Chowdhury and Pal, 1999; Dalton *et al.*, 2002; Masci *et al.*, 2004; Fuoss and Cathers, 1949; Costa and Vasconcelos, 2002), with a relative ratio between the initiator and the monomer

$$\frac{initiator}{monomer} = \frac{1}{10} .$$

The reaction is conducted in suspension,and initiated by the ions ce^{4+} (Hexanetratace rate of ammonium) $(NH_4)_2 [Ce(NO_3)_6]$ "Acros" leading first to the formation of a white- milky complex that disappears immediately, giving a radical (F) of Fucan to a proton (H$^+$) and an ion Ce^{3+},as it is shown in the following reaction equation :

Initiation:

$$F - H + Ce^{4+} \rightarrow [complex] \rightarrow F^{\cdot} + Ce^{3+} + H^+$$

Propagation:
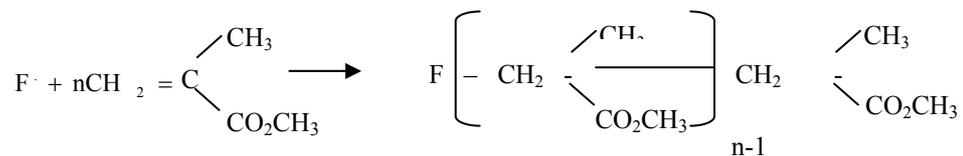
The kinetic study of this copolymerization, of which the polymerization rate measure is performed by pH metric measuring method -that we had put in evidence - and with comparison to the method of extraction by soxhelt with acetone.

2. Experimental Work

2.1 Products

Dextran of different molecular weights (MW= 10, 40, 70, 80.7, and 264 kg/mol) were purchased from Sigma for molecular weight assessment. Dextran (70 kg/mol) was also used for synthesis. It was dried in a vacuum oven at 60°C for 24h. Methyl methacrylate monomers were obtained from Acros France and were purified by washing with 5% NaOH and 20% NaCl, followed by distilled water. Ammonium cerium (IV) nitrate (Acros France) was dried at 80°C under vacuum for 24h. Solvents were of the highest commercially available purity.

Fucan N1 and Fucan BBP-2, having a mass of 95500g/mol and 46600g /mol respectively, are two fractions of Fucan obtained by HPLC chromatography on a S 5300 HR gel after an acidic extraction followed by an acidic hydrolysis (Hoppe HA, 1979), (see Figure 1).

The Dextran is, like the Fucan, soluble in water, whereas its copolymer with PMMA is soluble in the water /THF (20/ 80 v/v) mixture and in the dimethylsulfoxide (DMSO).

The polymerization of the methyl methacrylate « MMA »with Fucan N1 and Dextran T-70 depends closely on the concentration of the initiator (Colliec, 1993; Mulloy, B, 2002) of the monomer (MMA) and the concentration of the used polysaccharide.

This polymerization is performed by cycle –opening forming active radicals F or D that are likely to be bound by covalent links to the methyl poly-methacrylate (PMMA) forming Fucan copolymer(PMMA) and Dextran (PMMA).

This copolymerization is conducted in a highly acidic medium to avoid a possible formation of the ceric hydroxide, which can take place at a medium in which pH=4 to 5. In such a medium, the IR spectrum shows no anomaly.

The kinetic polymerization is performed by applying the PH- Metric measuring method, as an experimental technique, we know that the variation of the PH in the medium is linked to the initiator concentration at instant "t", with the equation:

$$[M]_t = [M]_0 \left(1 - \frac{\Delta C_t^H}{\Delta C_\infty^H} \right) \tag{1}$$

where : ΔC_t^H , et ΔC_∞^H - variation of the hydrogen concentration during the synthesis .

$$\Delta C_t^H = 10^{-pH_t} - 10^{-pH_0}$$

$$\Delta C_\infty^H = 10^{-pH_\omega} - 10^{-pH_0}$$

So we can write the equation (1) as follows :

$$[M]_t = [M]_0 \left(1 - \frac{10^{-pH_t} - 10^{-pH_0}}{10^{-pH_\infty} - 10^{-pH_0}} \right). \tag{2}$$

with pH_0, pH_t and pH_∞ are respectively the variation of the pH at the instant "t=0", at time t (we take

t=30mn) and the instant when the whole monomer will be converted into copolymer ($pH_\infty = pH_{cons\,tan\,t}$).

The equation (2) permits to determine directly the polymerization rate –Vp- ; monitoring the variation of the monomer concentration in function of pH, and time. We have also determined the polymerization rate by applying the extraction by soxhlet with the acetone method. We determined the percentage (P_g %) of the PMMA grafting, the grafting rate (Vg) of the copolymerization, polymerization, the homo –polymerization (V_h), and the total rate (V_P) of the polymerization that are calculated from the weight of the grafted poly-acrylic of the obtained products (Lepoutre P, 1975).

$$P_g\% = \frac{grafted \quad weight \quad of \quad PMMA \quad \times 100}{weight \quad of \quad polysaccha \quad ride} \tag{3}$$

$$V_g = \frac{grafted\ weight\ of\ PMMA \times 1000}{Mwde\ MMA \times reaction\ time(s) \times volume\ (ml)\ of\ reaction} \tag{4}$$

$$V_h = \frac{weight\ of\ homo - PMMA \times 1000}{Mwde\ MMA \times reaction\ time(s) \times volume\ (ml)\ of\ reaction} \tag{5}$$

The total rate of the polymerization is:

$$V_p = V_g + V_h \tag{6}$$

We have determined the polymerization rate-V_P-by applying two methods independent the one from the other (equations 2 and 6) (table III), for a comparison purpose.

2.2 Synthesis and Reaction of the copolymerization

In a (250 ml) reactor equipped with three flasks, we take a polysaccharide mass of 0, 5 to 1g (Fucan N1 or Dextran)dissolved in HNO_3 at 0, 2M. after 10minutes of agitation under an atmosphere of Argon (or N_2) at a temperature of 40 $\pm$ 1°C, we add at the same time $3,6.10^{-3}$M/L of cerium and 0,5M of MMA (of which the relative ratio $\frac{initiator}{Monomer} = \frac{1}{10}$), The time variation of the pH is measured at a sampling interval of 5mn. The reaction is considered finished when the pH does not change any more, and this is the case after 30 minutes of reaction ($pH_\infty = pH_{const}$).

The obtained product is poured into 500ml of methanol with the PH adjusted to a volume of 8, and NaOH at 10M. After that we concentrate the solution to a volume of 20/30ml approximately. We decant the solution into a spectra-membrane of a diameter of $\phi = 20,4mm$ to be cleaned /washed in EDTA solution at 0, 05 M during 72hours, under permanent agitation. Then, the solution is put under lyophilization, and later on in a vacuum dryer till a constant weight.

First of all, we have monitored pH evolution in time of the reaction medium of the copolymerization .This pH variation is generally not higher than the unity,as it is shown on Figure (2) bellow .

2.3 Extraction of Homo-polymer of PMMA

We weight exactly 2,00gr of each raw product- mentioned above – that was extracted with the acetone by soxhlet during 24 h, to eliminate the homo-polymer- poly (Methyl Methacrylate). The pure copolymer is dried at 50°C till a constant weight.

3. Characterization

3.1 Preparation OF Three- Dimensional Structures

We prepared discs or films by using dried homopolymer PMMA (15 mg) solubilized in THF. Copolymer DM was dissolved in 1 ml of THF/H_2O (80/20) that was treated in an ultrasonic bath for 1 h . Dextran gave any 3D structures. To obtain discs, solutions were poured in Petri dishes for 24 h at room temperature in a satured

atmosphere of THF and in the presence of $CaCl_2$ to absorb water. Thin films were stripped from the mold and were dried in an oven at $30°C$. A morphological analysis of the cross section of films was carried out by the of a Leica S-440scanning electron microscope (SEM) . All 3D structures were extensively washed with before any biological assays.

3.2 NMR Analysis

^{13}C NMR spectra of dextran, PMMA and copolymer DM were recorded by the use of a Varian Gemini 200 Mhz spectrometer in deutered dimethyl sulfoxide-d_6 at ambient temperature. Tetramethylsilane (TMS) was used as an internal standard. Before use, all products were lyophilized twice with deuterium oxide (D_2O).

3.3 Copolymers Analysis by Infrared Spectroscopy

This technique allows us to identify some chemical groupings that may be present in the polymers and the copolymers. Tablets of 150mg of potassium bromide (KBr), with infrared quality (Fluka).

The sample is mixed in the KBr, ground and then vacuum dried at 45°C during 6hours, pressed under 10 tons for 2minutes, and then stored at a 45°C in a humidity- free environment . These tablets are analyzed by means of a Fourier transform based infrared spectrophotometer (Perklin Elmer, 1600) .

Every spectrum is taken to be an average of the cumulus of 16 increments, in order to decrease the effect of background noise. Figure 3 shows the spectra of MMA, and Dextran taken individually, in addition to that of the synthesized Dextran-PMMA copolymer.

Curve (A) presents many strips characteristic of the PMMA : one at about $2953cm^{-1}$ which is assigned to the (CH_2) group, another strip is situated at $1732cm^{-1}$ which represents the carbonyl ($\rangle c = 0$) group and a third band is located at $1380cm^{-1}$ assigned to the(CH_3) Methyl group .

Curve (B) presents strips that are specific for Dextran T70: the presence of the radical (OH)is attested by the absorption band that appears at about $3400 \ cm^{-1}$, the strip at $2930cm^{-1}$ is assigned to the methylene group (CH_2), the strip arround1650corresponds to the grouping (OH) of the Dextran T70.

Curve (C) illustrates the spectrum of the product obtained by copolymerization of the Dextran and the MMA monomer by Cerium (Ce^{4+}). This spectrum presents strips that are common to both the Dextran and PMMA . We can notice an important intensity at $1733Cm^{-1}$ that corresponds to the carbonyl grouping ($\rangle c = 0$) .

Figure 4 shows that the individual Fucan N1 spectrum in curve (A) is identical to curve (B) with a concentration o f cerium $[Ce^{4+}] = 1,8.10^{-5} M / L$. Yet, when we increase the concentration of this latter 200 times, i.e. at $[Ce^{4+}] = 3,6.10^{-3} M / L$,by keeping the same concentration of monomer and polysaccharide,we notice the formation of a copolymer Fucan PMMA characterized by a peak located at $1725cm^{-1}$ for PMMA with respect to the spectrum of Fucan N1alone, as shown on curve (C).

3.4 Viscosity Measurements

In order to determine the molar mass of the different obtained products, we have measured the viscosity of Fucan N1, BBP-2 solutions as well as the viscosity of copolymer solutions for different cerium (Ce^{4+}) concentrations. In this technique, we use a well adapted viscometer (the Ubbelohde Viscometer) with a capillary diameter of 0,7mm, was used for two different polysaccharides; Fucan N1 and Fucan BBP-2 having a mass 95500 g/mol and 46600g/mol respectively

We determine $\left(\frac{ln\eta_2}{C} \right) = \left[\frac{ln(t/t_0)}{C} \right]$ and the specific viscosity $\frac{\eta_{sp}}{C} = (t - t_0)/t_0 C$ for a set of an increasing

concentration in the percentage of Fucan N1 and BBP-2 dissolved in water, as follows (0% , 0, 45 %, 0,65%, 0, 75%, 1,0%, 1,25%, 1,45%, 1,65%, and 2 %).

On the same graph ($\frac{ln\eta_r}{C}$), we have simultaneously plotted the specific viscosity ($\frac{\eta_{sp}}{C}$) in function of

polysaccharide concentration. The intrinsic viscosity $[\eta]$ is obtained by extrapolation and intersections of these

two curves at a zero-point concentration .On the other hand, this intrinsic viscosity is related to the molar mass

through the formula of Mark Houwkin: $[\eta] = K.M^a$, where a and K are constants.

As for the two fractions of Fucan N1 and BBP-2 with known mass, the values of the constants were deduced from measures of the intrinsic viscosity $[\eta]$ at a zero-point concentration. For example, as concerns the first fraction $[\eta_1] = 0,252$ and $[\eta_2] = 0,086$, we find Fucan values as follows:

$$\left| \begin{array}{l} a = 1,49 \\ K = 8,8.10^{-9} \, dl \, / \, g \end{array} \right.$$

And for the Dextran T70 (with a mass=73 000g/mol), in water and in DMSO, we have found the following values:

$$\left| \begin{array}{l} a = 0,50 \\ K = 98,8.10^{-5} \, dl \, / \, g \end{array} \right.$$

The difference in values of 'a' for the Dextran T70 and Fucan, is present only in aqueous solutions, the Dextran is manifested therefore, more flexible than the Fucan.

3.4.1 Viscosity and mass measurements of the obtained copolymers

The measurement of the molar mass by applying the viscometric method is performed through measuring the intrinsic viscosity by extrapolation of the two curves at $[\ln \eta_2] / C$ and $\dfrac{\eta_{sp}}{C}$ at a zero –point concentration.

This is why we have synthesized tow Fucan PMMA copolymers; one with no monomer ; the other with the presence of 0,4% of monomer MMA, keeping the same concentration values in the initiator and the polysaccharide (0,5 of Fucan), soluble in the mixture water/ THF (20/80 v/v) at T° = 40°C.

We found the intrinsic viscosity equal to 0,16 dl/g for the first copolymer, but equal to 0,244 dl/g, for the second copolymer .The viscometric mass Mv corresponding to the viscosity could be formulated through the following equation :

$$\ln [\eta] = \ln \left[8,8.10^{-9} \right] + 1,49 \ln \overline{M} \tag{7}$$

where

$$[\eta] = 0,244; \qquad \overline{M} = 98900 g / mol$$

$$[\eta] = 0,16; \qquad \overline{M} = 64800 g / mol$$

We notice that the increase of the viscosimetric mass is due to the increase of PMMA formed in shapes of grafted connections on the polysaccharide, on the one hand, and this prove the effective formation of a copolymer between the Fucan and PMMA for Dextran T70, on the other hand. We can use the following formula:

$$\ln [\eta] = \ln \left[98,8.10^{-5} \right] + 0,50 \ln \overline{M} \tag{8}$$

By the same manner, knowing $[\eta]$ we can deduce the molar mass $\overline{M}$.

3.4.2 Determination of the obtained copolymers by HPLC in function of initiator concentration [CAN] ^{½}

$\overline{M}_v$ determination of the obtained copolymers by HPLC chromatography on a S 5300 HR gel, shows that those ones decrease as the initiator concentration increases, i.e.:

For $[CAN]^{1/2} = 3.10^{-2} M / L$ we have $\overline{M} = 1,28.10^{5} g / mol$

And for $[CAN]^{1/2} = 6.10^{-2} M / L$ we have $\overline{M} = 0,59.10^{5} g / mol$

We can interpret these results on Figure 5.

As for the case of Dextran, the Fucan mass decreases because of an acid hydrolysis of the macromolecular chains during the different stages of synthesis. We can notice clearly that this mass variation could be interpreted in the following formula:

$$\overline{M} = \frac{3,74.10^3}{\left[Ce^{+4}\right]^{1/2}} \tag{9}$$

$\left[CAN\right]^{1/2}.10^2 \, mol/l : 0,9 \, ; \, 3 \, ; \, 3,46 \, ; \, 4,59 \, ; \, 6,00$

$\overline{M} : g/mol : 4,0.10^5 \, ; \, 1,28.10^5 \, ; \, 1,047.10^5 \, ; \, 0,87.10^5 \, ; \, 0,59.10^5$

4. Results and Discussion

This research consists of applying the pH-metric measuring method in the kinetic study the MMA polymerization of the methacrylate methyl, with the polysaccharides Fucan N1 and Dextran T70, in presence of ceric ions (Ce^{4+}) in the best conditions .We must take the quantity of the initiator and the monomer in a reactor we have found equal to 1/10.

The infrared analysis (IR)of the copolymers obtained after radical synthesis, shows that the polymerization depends on the nature of each polysaccharide, and on the concentration of the cerium (Ce^{4+}) , and the monomer used ; the reaction of the polysaccharide / poly acrylic synthesis is performed through several stages, as depicted on the following graph (Mansor A, 2000):

Stage 1: Formation of radical I
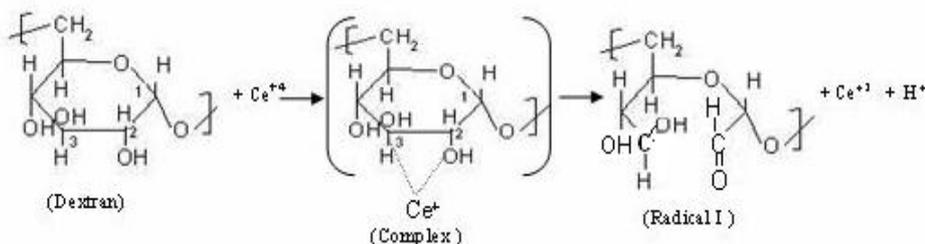
Stage 2: Formation of the Oxidum
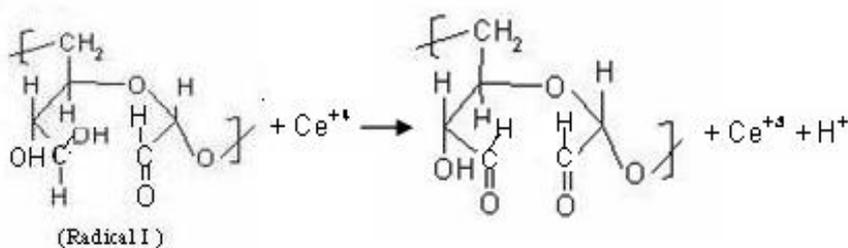
Stage 3: Formation of radical II

(Radical II)   (Monomer)   (Copolymer)
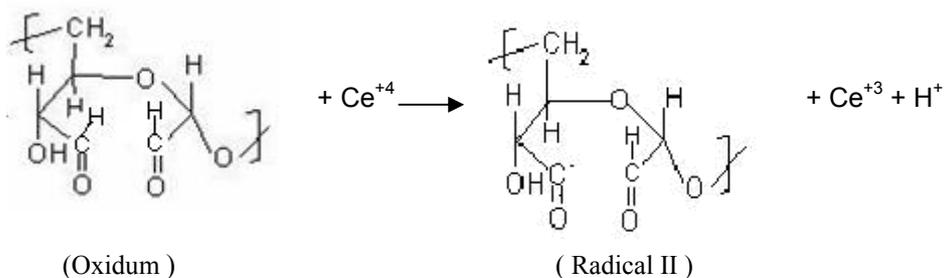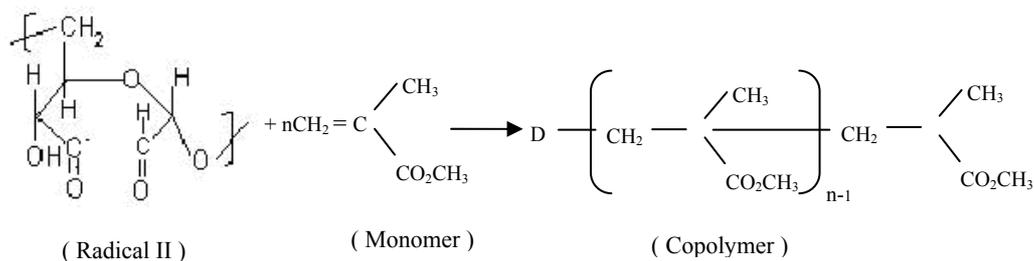
The radical II is chained to the monomer and engendering copolymers. The first stage consists of forming a complex between the polysaccharide and the cerium (Ce^{4+}). This complication is performed between the cerium (Ce^{4+}) and hydroxide groups in position 2 and 3 of the Polysaccharide. After a laps of time, it is decomposed giving a Radical I, ion Ce^{3+} and a proton H^+. The second stage, however, consists of forming an oxydium from a radical I with the cerium, making the appearance of aldhydic groups in position 2 and 3 of the polysaccharide, an ion Ce^{4+} and a proton H^+. As concerns the third stage, it consists of forming a radical II, which is Dextran radical (D or F) responsible for the propagation with the monomer $(D^{\cdot} + M_n \rightarrow DM_n^{\cdot})$ this radical $(D^{\cdot})$ is generated by the reaction between Oxidium and Cerium (Ce^{4+}).

The termination is achieved by classical termination.

$$DM^{\cdot} + DM^{\cdot} \rightarrow Copolymer$$

Or: $FM^{\cdot} + FM^{\cdot} \rightarrow Copolymer$
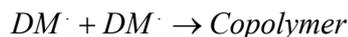
The analysis of ^{13}C NMR spectrum (Fig. 6.) suggests a chemical structure of Dextran-PMMA polymer as indicated in (Chauvièrre C, 2003).

Under the light of the obtained results and the discussion we have led, we may establish that our polymerization follows a reactional mechanism a little complex; the stages of which are governed by the following reaction equation:

Initiation:

$$F-H+Ce^{4+} \xleftrightarrow{K} [Complex] \xrightarrow{k_0} F^{\cdot} + Ce^{3+} + H^+ \tag{10}$$

$$F^{\cdot} + M \xrightarrow{k_0} FM \tag{11}$$

$$M + Ce^{4+} \xrightarrow{k_1} M^{\cdot} + Ce^{+3} + H^+ \tag{12}$$

$$F^{\cdot} + Ce^{4+} \xrightarrow{k_2} F-OX + Ce^{3+} + H^+ \tag{13}$$

$$F-OX + Ce^{4+} \xrightarrow{k_3} F^{\cdot} + Ce^{3+} + H^+ \tag{14}$$

Propagation :

$$FM^{\cdot} + M_n \xrightarrow{k_p} FM_{n+1} \tag{15}$$

$$M^{\cdot} + M_n \xrightarrow{k_p} M^{\cdot}_{n+1}$$

Termination :

(17)

$$FM\dot{}_{n} + FM\dot{}_{m} \xrightarrow{k_t} FM_{n+m}F$$

(18)

$$FM\dot{} + M\dot{} \xrightarrow{k_{t_1}} FM_{n+1}$$

$$M\dot{}_{n} + M\dot{}_{m} \xrightarrow{k_{t2}} M_{n+m}$$
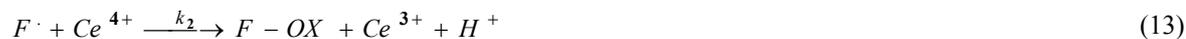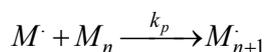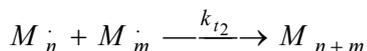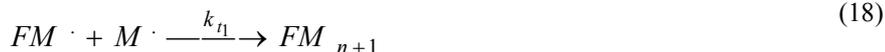
To put in evidence this polymerization mechanism,we should suppose that the states between the following different initiating species,are quasi-stationary . That is to say:

$$\frac{d[F\dot{}]}{dt} = Kk_0[F][Ce^{4+}] + k_3[Ce][F-OX] - k_a[F\dot{}][M] - k_2[F\dot{}][Ce] = 0 \qquad (20)$$

$$\frac{d[FM\dot{}]}{dt} = k_a[F\dot{}][M] - k_k[FM\dot{}]^2 - k_{t_1}[FM\dot{}][M\dot{}] = 0$$

$$\frac{d[M\dot{}]}{dt} = k_1[Ce][M] - k_{t_1}[FM\dot{}][M\dot{}] - k_{t_2}[M\dot{}]^2 = 0 \qquad (21)$$

$$\frac{d[F-OX]}{dt} = k_2[F\dot{}][Ce^{4+}] - k_3[Ce^{4+}][F-OX] = 0 \qquad (22)$$

By summing together the equations (20to23) and ignoring the equation (22) which is less likely to take place; because we did not notice any considerable attack by the cerium (Ce^{4+}) on the monomer . By assuming that the termination constants are equal to the global $k_t (k_t = k_{t_1} = k_{t_2})$ (Mansor A, 2000), we obtain that:

$$Kk_0[F][Ce^{4+}] - k_t[FM\dot{}]^2 - 2k_t[FM\dot{}][M\dot{}] - k_t[M\dot{}]^2 = 0 \qquad (24)$$

$$Kk_0[F][Ce^{4+}] = k_t([FM\dot{}] + [M\dot{}])^2$$

We deduce:

$$[FM\dot{}] + [M\dot{}] = (Kk_0[F][Ce^{4+}]/k_t)^{1/2} \qquad (25)$$

The polymerization rate Rp of the Fucan N1 or Dextran in presence of a ceric initiator, is expressed in this formula:

$$R_p = k_p[FM\dot{}][M] + k_p[M\dot{}][M] = k_p([FM\dot{}] + [M\dot{}])[M] \qquad (26)$$

By substituting the expression of eq. (25) into eq. (26), we obtain:

$$R_p = k_p \left(\frac{Kk_0}{k_t}\right)^{1/2} \cdot [F]^{1/2}[Ce^{4+}]^{1/2}[M] \qquad (27)$$

The expression of the polymerization rate Rp of the Fucan N1 and Dextran T70 with the MMA in presence of a ceric salt used as initiator, in acidic medium a simple ratio between Rp and the order equal to the concentration unity of the monomer MMA, and to the square –root of both the polysaccharide and initiator (Figures 7 to 10).

And also, the speed of polymerization is:

$$R_h = R_p/2 + K[Ce^{+4}]_{max} \qquad (28)$$

The grafting speed is expressed as:

$$R_g = R_p/2 - K[Ce^{+4}]_{max} \qquad (29)$$

Consequently, the rate of grafting is given by :

$$PG\% = (AR^2_P + BR_P + C).100 \qquad (30)$$

where A, B,C and K are constants which can be determined ultimately.

We also know that the speed of polymerization 'R_p' is proportional to the square-root of initiator concentration $R_P = K'[Ce^{+}4]^{1/2}$, and the same relationship is found for the quantities R_h , R_g and PG.

The method applied in measuring the polymerization rate (Rp) is the PH-metric measuring method, compared to the extraction by soxhlet with the acetone (method of " Le Poutre and Hui (1975) (see Table III).

5. Reliability Control of the PH-Metric Method

In order to control the reliability of the PH-metric method, we compared it to a more exact and precise method; which is the "extraction by soxhlet with the acetone method. By comparing these two methods, we can see that same values of PG, V_g, V_h and the universal constants A, B, C and K are exactly found by both methods. The variation of PG reaches the same maximum for a maximal speed of $R_p = 3,39. 10^{-5}$ mol.l^{-1}.s^{-1} and a initiator concentration [CAN] $=1,197. 10^{-3}$ M for both methods . The obtained results are given in the following table (see Table III). We notice that the pH-metric method is in good concordance with the extraction by soxhlet with the acetone method, at strong concentration values of the initiator.

$R_p^{(a)}$, $R^{(a)}{}_h$, $R^{(a)}{}_g$ and $PG^{(a)}$ polymerization rate determined by the pH-metric method, that we have worked out .

As Figures (7 -10) show, the quantity kp $(kk_0/k_t)^{1/2}$ is equal to $=5,32$; $10,22$ and to $13,71$ for soluble starch (Mansor and Haron, 2000) ; as concerns Dextran T70 and Fucan N1 respectively . This quality varies increasingly with a rate of nearly 2.5 when going from the soluble starch to the Fucan and this in proportion with the mass of each polysaccharide used, namely :

$M_n = (164,4)_n$ g / mol For the soluble starch ; 73000g/ mol for the Dextran T70,and finally 95500g/ mol for the Fucan N1 .

6. Conclusion

We can summarize the obtained results in the following points:

Polymerization between polysaccharides and poly-acrylics is generally achieved through opening the polysaccharide cycle. This kinetic polymerization is considered to be a complex one. The pH-metric method used to determine Rp is found to be very precise and with great concordance with the extraction by the acetone method . The infrared spectroscopy shows that the copolymer can't be formed if the initiator concentration is less than $[CAN] = 1,8.10^{-5} M /l$,but when this latter is increased to 200 times,we notice the formation a copolymer characterized by a peak situated at 1725cm^{-1} for PMMA on the polysaccharide spectrum alone, with an $[MAM] = 0,4\%$. The viscometry shows the effective formation of a copolymer between the polysaccharide and the PMMA, due to the intrinsic viscosity increase of 0,16 dl/g to 0,244dl/g in absence and presence of 0,4 % of monomer . The polymerization rate Rp of polysaccharide / poly-acrylic depends on a kinetic complex, first order,equal to the concentration of the monomer and, and to the square-root of the initiator and polysaccharide.

The grafting rate of PMMA (PG%) on the polysaccharide increases with the increase of (CAN) concentration, it reaches a maximum concentration equal to : [CAN] =1,197 . 10^{-3} Mol/l, and realizes 196,.60% (this maximum value is found to be equal to 260% at 0.5.10^{-3} M/l ceric ion).

Regarding difficulties that may face researchers for determining the speed of polymerization R_P, we propose to use the pH-metric method because it is simple and precise, and also does not require sophisticated means. In addition, it opens doors for great perspectives in this domain of research.

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Table 1. Measurement of the relative viscosity $\left(\frac{ln\,\eta_r}{C}\right)$ and specific viscosity $\left(\frac{\eta_{sp}}{C}\right)$ of Fucane N1 in function

of its concentration percentage in the solvent H_2O at a temperature T°=40°C

$[Fucan\ N1]$%	0	0,45	0,65	0,75	1,0	1,25	1,45	1,65	2,0
$\dfrac{\ln\eta_r}{C}$	0,252	0,260	0,265	0,280	0,300	0,305	0,310	0,320	-
$\dfrac{\eta_{sp}}{C}$	0,252	0,280	0,320	0,340	0,350	0,360	0,380	0,410	-

Table 2. Measurement of the relative viscosity $\left(\frac{ln\,\eta_r}{C}\right)$ and specific viscosity $\left(\frac{\eta_{sp}}{C}\right)$ BBP-2 in function of its

concentration percentage in the solvent H_2O at a temperature T°=40°C

$[BBP-2]$%	0	0,45	0,65	0,75	1,0	1,25	1,45	1,65	2,0
$\dfrac{\ln\eta_r}{C}$	0,086	0,10	0,11	0,12	0,13	0,14	0,15	0,165	-
$\dfrac{\eta_{sp}}{C}$	0,086	0,11	0,12	0,13	0,14	0,16	0,17	0,185	-

Table 3. Comparative table of the two (Vp) measuring methods: the pH- metric method and the extraction by soxhlet with the acetone method .

$[CAN]^{1/2}.10^2 M/1$	2	3	3,46	4,59	5,99
PG %	145,30	163,05	218,10	201,.20	16,220
$R_h.10^5 mol/l^{-1}s^{-1}$	/	1,476	1,504	2,272	3,084
$R_g.10^5 mol/l^{-1}s^{-1}$	/	1,004	1,256	1,868	2,436
$R_p=(R_h+R_g).10^5 mol.l^{-1}s^{-1}$	/	2,480	2,760	4,140	5,518
$R_p^{(a)}. \quad 10^5$ mol.l^{-1}.s^{-1}	2,25	2,660	3,040	4,000	5,520
PG$^{(a)}$%=(-4,084.10^{9}R^2_P+2,774.10^{5}R$_P$-2,698). 100 or $= K^{'}[Ce^{+4}]+K^{''}[Ce^{+4}]^{1/2}+K^{'''}$	147,75	179,31	196,29	186,68	17,58
R$^{(a)}_g$=(R$_P$/2 - 2,71 . 10^{-3}[Ce^{+4}]$_{max}$). 10^5 Mol. L^{-1}. s^{-1}	/	1,006	1,196	1,676	2,436
R$^{'a)}_h$=(R$_p$/2 + 2,71 . 10^{-3}[Ce^{+4}]$_{max}$) . 10^5 mol.l^{-1}.s^{-1}	/	1,654	1,844	2,324	3,084

seaweed (Thalles) $\xrightarrow{(1)}$ Parietal material $\xrightarrow{(2)}$ Raw acidic extract $\xrightarrow{(3)}$ Fucans.

1- Preprocess, Extraction.

2- Hydrolysis.

3- Deterioration, fractioning.

Figure 1. Simplified flow- chart of Fucans
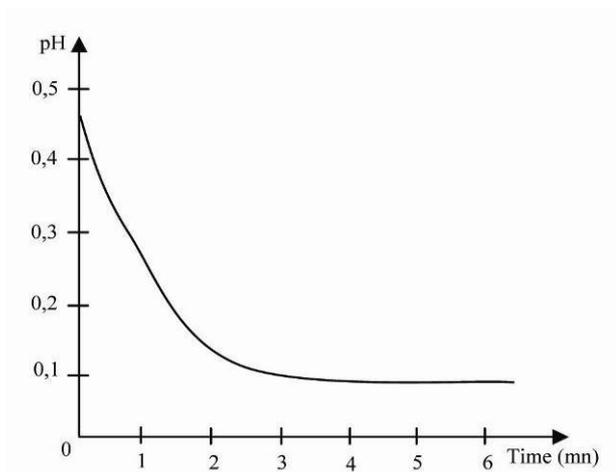
Figure 2. pH evolution during synthesis reaction of the copolymer
Fucan PMMA; Temperature :40°C; solvation HNO_3 at 0,2 M
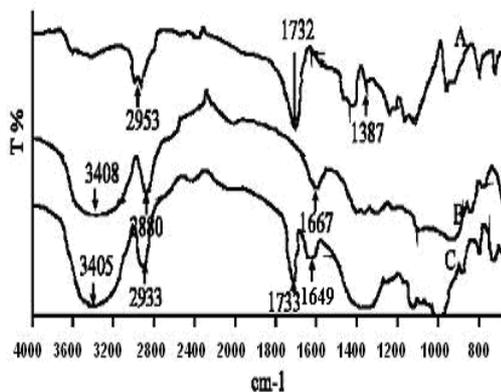
Figure 3. Infrared spectrum of copolymer Dextran –PMMA;
Curve (A) PMMA alone; Curve (B) Dextran alone;
Curve(C) copolymer of Dextran ; 0,5g ; MMA 2%;
Cerium $3,6.10^{-3}$ M.
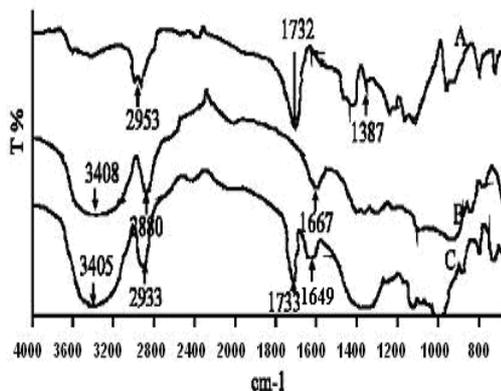
Figure 4. Infrared spectrum of copolymer Fucane –PMMA;
Curve (A) Fucane alone; Curve (B) 0,5 g of Fucane,
0, 2% of MAM ,Ce^{+4} $1,80.10^{-5}$ g/mol;
Curve(C) 0,5g of Fucane, 0,2% of MMA, Ce^{+4} $3,6.10^{-3}$g /mol
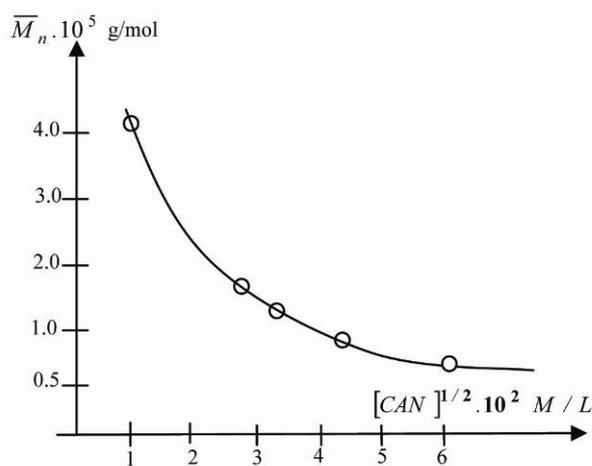
Figure 5. Variation of the copolymer mass obtained by HPLC in function of the monomer concentration $[CAN]10^2 \ M/L$
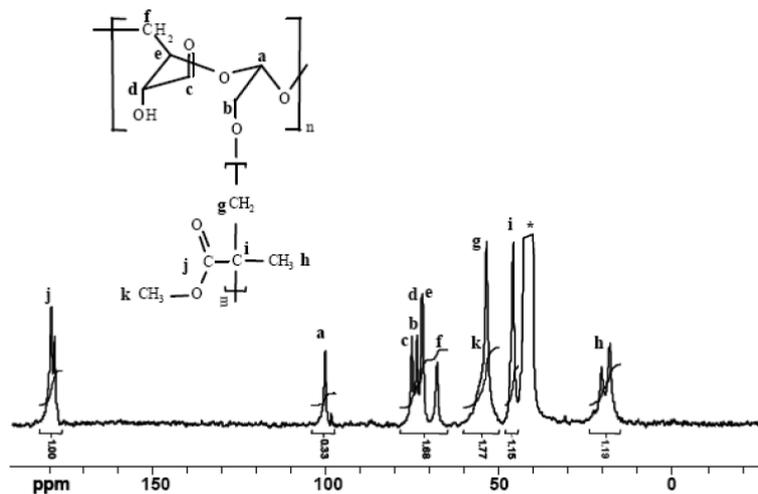
Figure 6. The ^{13}C NMR spectrum of DEXTRAN-PMMA in deutered DMSO. Carbon atoms and corresponding peaks are identified by a literal
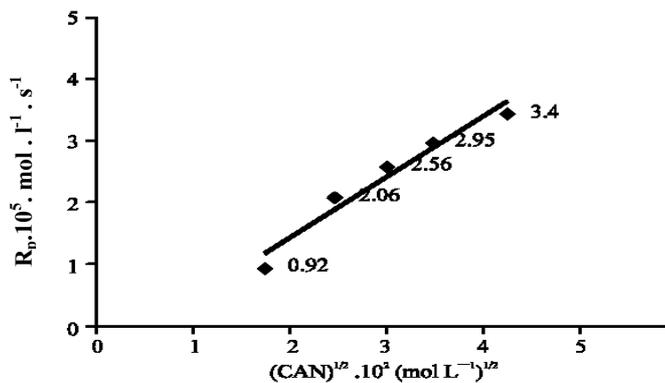
Figure 7. Polymerization rate (Rp) of Fucan in function of the square-root of CAN;
MMA=0,0742M; (Fu)=00417g; (HNo3)= 0,2M ; temperature =40°
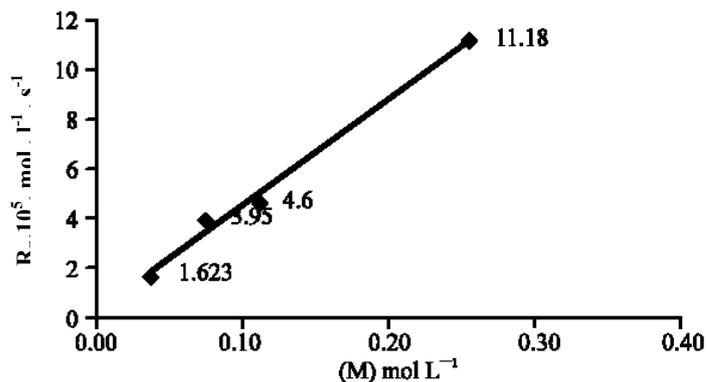
Figure 8. Polymerization rate (Rp) of fucan N1 with MMA in function of monomer;
(Fu) =00417g ; (CAN)=0,503.10^{-3}M, (HNo$_3$)= 0,2M , temperature = 40°C
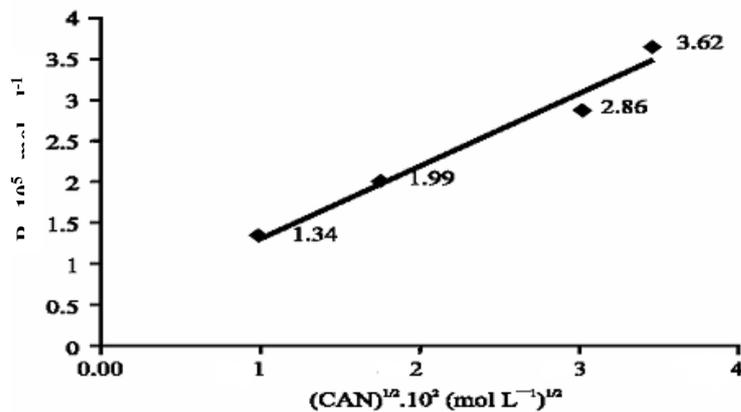
Figure 9. Polymerization rate (Rp) of fucan N1 with MMA in function of the square root of the initiators (CAN),
Dextran= 0,0318g; (MMA) = 0,0742M (HNO$_3$) = 0,2M Température = 40°C
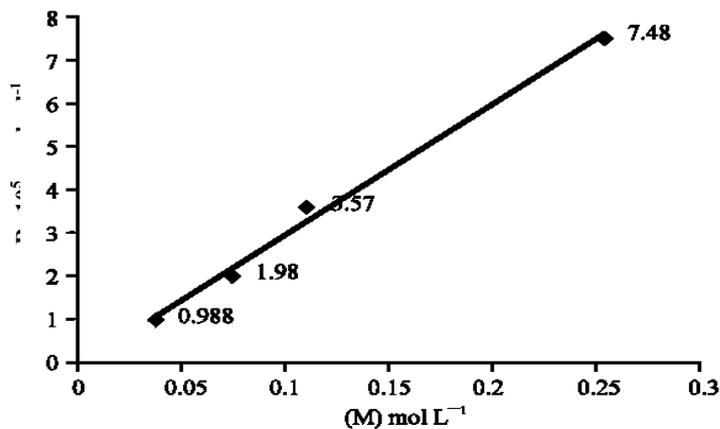
Figure 10. Polymerization rate (Rp) of fucan N1 with MMA in function of monomer concentration (M),
Dextrane= 0,0318g ; (CAN) = 0,503.10^{-3} M, (HNO$_3$) = 0,2M Temperature = 40°C