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Amphiphilic derivatives of chitosan using microwave irradiation. Toward an eco-friendly process to chitosan derivatives☆

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ABSTRACT

Conventional heating and microwave irradiation have been compared for the synthesis of chitosans grafted with alkyl chains. Reaction time (1–60 min), temperature (25 and 40 °C) and chitosan molar mass have been studied onto the yield of alkylation. The irradiation mode has been scrupulously controlled to highlight the effect of the use of microwaves. The chemical structure of modified polymers (degree of alkylation) is determined from NMR. In relation to the rheological behavior and surface tension measurements, the evolution of hydrophobic interactions is studied as a function of the yield of alkylation. A maximum of intrinsic viscosity and hydrodynamic diameter was observed for a degree of alkylation of around 10%. All the results tend to prove that microwave assisted synthesis is a powerful method to obtain modified chitosan under extremely low reaction time without any degradation and/or property modifications.

1. Introduction

Chitosan is a *N*-deacetylated derivative of chitin, which is one of the most abundant organic materials, found in crustacean, mollusks and insects where it is an important constituent of the exoskeleton. Chitosan (Chi) is biodegradable, biocompatible, non-irritant (Gupta & Jabrail, 2007) and exhibits good film-forming properties and high mechanical strength and adhesion (Mucha, Wankowicz, & Balcerzak, 2007; Wang, Zhang, Cheng, & Dong, 2000). All these characteristics make it suitable for a wide range of applications such as controlled delivery systems (Gupta & Ravikumar, 2000; Hejazi & Amiji, 2004; Illum, 1998; Shiraishi, Imai, & Otagiri, 1993), wastewater treatments (Baroni, Vieira, Meneghetti, da Silva, & Beppu, 2008; Crini, 2006), packaging (Arvanitoyannis, Nakayama, & Aiba, 1998; Arvanitoyannis, 1999; Tual, Espuche, Escoubes, & Domard, 2000), separation membranes (Beppu, Vieira, Aimoli, & Santana, 2007; Won, Feng, & Lawless, 2002), biosensors (Coche-Guerente et al., 2005; Tsai, Chen, & Liaw, 2007; Wu et al., 2007).

However to improve its physico-chemical properties and widen the domain of applications it is possible to modify its structure due to the presence of hydroxyl and amino groups on the macromolecular chain. The presence of amino groups gives the opportunity of specific reactions such as N-alkylation, N-carboxylation or crosslinking . . .

N-alkylation allows preparing amphiphilic derivatives of chitosan which possess specific properties such as rheological (and their autoassociative character) (Desbrieres, 2004) or surface active characteristics (Babak, Rinaudo, Desbrieres, Vikhoreva, & Michalski, 1997). This class of polymers has found a widespread use in technical formulations. Their main function is as rheology modifiers (particularly thickening agents) especially in aqueous based formulations within numerous industrial domains such as paints, oil recovery, cosmetic or foods (Glass, 1996), or emulsion stabilizers (Carrier, Covis, Marie, & Durand, 2011). However their elaboration process presents disadvantages considering environmental point of view either from the energy needs or the number and/or nature of chemicals involved.

In 1986, Gedye et al. (1986) and Giguere, Bray, Duncan, and Majetich (1986) were the first to describe the use of microwave oven as an efficient tool in chemical synthesis. Further works were described later (Delgado et al., 1992; Villemin & Labiad, 1992; Raner & Strauss, 1992) the article number per year continuously increased from the 1990s. Microwave heating is a process within a family of electroheat techniques that utilize specific parts of the electromagnetic spectrum and may be used as an alternative heating method. It has therefore gained interest in organic syntheses before to be applied for polymer synthesis and modification. First experiments

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on a microwave-assisted radical polymerization of styrene were done from 1993 (Chia, Jacob, & Boey, 1996; Palacios & Valverde, 1996). Numbers of studies have been published on microwave-assisted syntheses since these first successful results.

Until late 1990s, the absence of temperature control or the use of domestic ovens characterized the majority of published microwave-assisted chemistry and was responsible of uncontrolled reactions and of the lack of reproducibility. For a better understanding and safety reasons, more reliable equipment with proper control over temperature and pressure have been developed and used by scientists within the laboratories (Kappe, 2004). The high performance microwave reactor specially designed for synthesis applications in research and development laboratories offers now unique properties, which are unattainable by utilizing conventional reaction vessels. In particular, they enable extremely rapid heat transfer, volumetric and selective heating, compactness of equipment, speed of switching on and off and pollution-free environment as there are no products of combustion. Two types of microwave reactors are nowadays available for chemists; multimode and mono-mode (or single-mode). Within the latter, the electromagnetic beam is focused and located in the center of the reaction vessel. This enables the reactive medium to be placed in the position of maximum electric field for optimum transfer of the electromagnetic energy (Hayes, 2002). Based on these recent developments, a rapidly increasing variety of applications in different areas of polymer chemistry has been established to date (Bardts, Gonsior, & Ritter, 2008; Hoogenboom & Schubert, 2009; Kempe, Becer, & Schubert, 2011). Among these different areas are ring opening polymerization (Sinnwell & Ritter, 2006), peptide synthesis (Bacsa, Desai, Dibo, & Kappe, 2006), click chemistry (Malkoch et al., 2005) and controlled radical polymerization (Rigolini, Grassl, Billon, Reynaud, & Donard, 2009).

First papers on the modification of polysaccharides using microwave irradiation were published in beginning 2000s (Cao, Ge, & Lai, 2001; Singh, Sethi, Tewari, Srivastava, & Sanghi, 2003; Singh, Tiwari, Tripathi, & Malviya, 2003) and grafting reactions were specifically concerned (Nayak & Singh, 2001; Singh, Kumar, & Sanghi, 2012). Cellulose (Matahwa, Ramiah, Jarrett, Mcleary, & Sanderson, 2007; Mishra, Rani, & Sen, 2012), starch (Horchani, Chaâbouni, Gargouri, & Sayari, 2010; Singh, Tiwari, Pandey, & Singh, 2007)... were the most commonly used polysaccharides for reactions such as grafting of synthetic polymers on the macromolecular backbone or on fibers (Kaith, Jindal, Jana, & Mithu Maiti, 2009). But other reactions were performed on polysaccharides as desulfation (Navarro, Flores, & Stortz, 2007) or synthesis of modified pectins (Calce, Bugattin Vittoria, & De Luca, 2012) and degradation of hyaluronan to prepare low molecular weight samples (Drimalova, Velebny, Sasinkova, Hromadkova, & Ebrinerova, 2005) were also performed using microwave irradiation.

Chitosan can be specifically modified due to the presence of amino groups within the macromolecular backbone. Some of these modifications were carried out using this process (Huacai, Wan, & Dengke, 2006; Liu, Li, Fang, & Chen, 2005; Liu, Li, Li, & Fang, 2004) but few papers compare microwave irradiation and conventional heating performed in well-controlled conditions.

This manuscript presents for the first time the use of microwave irradiation for grafting alkyl chains on chitosan and the comparison with conventional heating.

2. Experimental methods

2.1. Materials

Two samples (#1 and #2) of chitosan (Chi) were provided from Sigma–Aldrich and respectively exhibit viscosity-average molar masses of 70,000 (Chi1) and 210,000 (Chi2) g mol^{-1} and degrees of acetylation of 5% and 25% respectively. The average viscometric molar mass was estimated from the intrinsic viscosity determined in the solvent 0.3 M CH_3COOH (AcOH)/0.2 M CH_3COONa (AcONa) (pH 4.4) using the Mark Houwink parameters in relation with the degrees of acetylation of samples we used (Rinaudo, Milas, & Le Dung, 1993). The degree of acetylation was determined by ^{1}H NMR, generally considered as the most sensitive technique (Rinaudo, Le Dung, Gey, & Milas, 1992).

Octanal (Aldrich; CAS 124-13-0), sodium cyanoborohydride (Aldrich; CAS 25895-60-7) and solvents were used as received.

Deionized water, with a resistivity of 18.3 MΩ cm at 25 °C, was filtered through a 0.22 μm Millipore filter prior to use.

2.2. Techniques

2.2.1. NMR spectroscopy

^{1}H NMR spectra were recorded at 85 °C on a Bruker Avance 400 NMR spectrometer in D_2O in which a few drops of 1 M HCl were added (pH around 4). The number of scans was 64 and the latency time equal to 5 s. The chemical shifts were referred to the residual solvent peak. Polymer concentration was 10 mg mL^{-1}. The degree of acetylation was determined from the integral of the CH_3 signal at 1.97 ppm compared with the integral of H-1 protons considered as an internal standard (Desbrieres, Martinez, & Rinaudo, 1996).

2.2.2. Viscosimetry

Intrinsic viscosity for molar mass determination was measured using a AMVn ball viscometer from Anton Paar at 25 °C. The solvent is 0.3 M AcOH/0.2 M AcONa and it was calibrated with deionized water using angles between 15° and 90°.

The role of the hydrophobic interactions was studied using the 0.3 M AcOH/0.05 M AcONa (pH 3.82) solvent to decrease the role of the salt, known to modify these interactions in relation with Hofmeister series (Hofmeister, 1888).

Solutions were filtered with 0.45 μm membranes before experiments and the absence of aggregates was considered from weighing the membrane.

2.2.3. Rheology

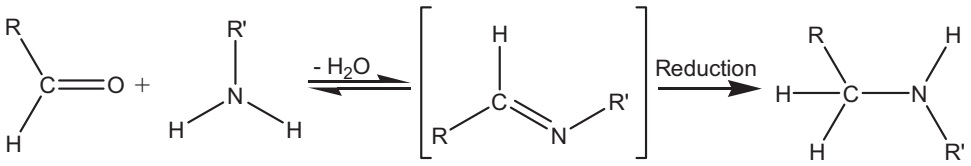
Rheological experiments were carried out at 25 °C on a Bohlin Gemini 2 rheometer from Malvern using a Couette geometry. The shear rate ramp was performed using an increasing-decreasing mode at imposed strain. The solutions were prepared in 0.2 M AcOH/0.05 M AcONa (pH 4.03) solvent at a polymer concentration equal to 10 g L^{-1}, larger than the overlapping concentration.

2.2.4. Dynamic light scattering

Dynamic light scattering experiments were performed using a DL135 apparatus from Cordouan Technologies (France). Polymer concentrations were 10 g L^{-1} in 0.2 M AcOH or 0.2 M AcOH/0.05 M AcONa (pH 4.03) solvents.

2.2.5. Tensiometry

A drop tensiometer (Tracker, Teclis, France) was used to measure the surface tension by analyzing the axial symmetric shape (Laplace profile) of the rising bubble in aqueous polymer solution (Nagarajan & Wasan, 1993; Saulnier et al., 2001). All the measurements were performed at a controlled temperature (25 °C) with a constant area of the air bubble. Polymer solution concentrations were 1 g L^{-1} in 0.2 M AcOH/0.05 M AcONa (pH 4.03).



Scheme 1. Synthesis of amphiphilic derivative of chitosan.

2.3. Synthesis of amphiphilic alkylated chitosan

The alkylated chitosan derivatives were obtained by reductive amination following the procedure described by Yalpani and Hall (1984). The scheme of the reaction is given in Scheme 1.

It is a versatile and specific method for creating a covalent bond between a substrate and the amine function of the chitosan. Within the present work it involves the reaction between the amine function of the glucosamine unit and an aldehyde function. Generally the reaction of substitution on polysaccharides proceeds in heterogeneous conditions with preferential reactivity of accessible zones thus giving a blockwise distribution of substituents. Hence the derivative is structurally inhomogeneous. We have developed a procedure for performing homogeneous chemical reactions in acidic medium, which allows a better accessibility of reactive sites (Desbrieres et al., 1996) and a homogeneous distribution of substituted units along the macromolecular chain. The reaction is performed in mild conditions with no modification of the acetylation nor the polymerization degrees. On the basis of chitosan, the amine protonation in acidic condition gives cationic amphiphilic polymers. Octanal was chosen to be the aldehyde grafted on the chitosan chain because a minimum of 6 carbon atoms are necessary to observe rheological hydrophobic effects (Desbrieres et al., 1996) and we have to take into account the solubility of the amphiphilic derivatives when the degree of alkylation is increasing when long alkyl chains are grafted.

Two types of process have been used to keep the temperature constant: the conventional heating using a jacketed reactor or microwave irradiation. In all the cases the reaction was carried out in a 100 mL one-necked round bottom flask capped with a rubber septum. Typically 12 g of ethanol were added to 25 mL of chitosan solution (around 15 mg of chitosan per mL of 0.2 M acetic acid) with different volumes of octanal solution in ethanol to reach the adequate composition (in relation with the required degree of alkylation) and excess of sodium cyanoborohydride ($n_{NaCNBH3}$/monomol$_{Chi}$ = 3). Reactions were carried out at 25 or 40 °C (all the chemicals were prepared at used temperature to avoid equilibrium time in the reactive medium) and reaction time range from one minute to one hour. The obtained derivative was precipitated in 10% NaOH solution (final pH around 8.5) and washed several times in ethanol/water (70/30, vol) up to the centrifugation supernatant had a conductivity value lower than a few dozens of μS cm^{-1}, corresponding to salt concentration smaller than 10^{-3} mol L^{-1}. Last washing of the precipitate was performed in pure ethanol.

A Discover Proteomics single-mode synthesizer from CEM Corp was used. This apparatus uses a frequency of 2.45 GHz and power up to 300 W. It allows controlling many parameters as temperature, irradiation power, air cooling and stirring.

To compare the two modes of synthesis (conventional and microwave heating) the yield was defined according to the relation:

$$\text{Yield} = \left(\frac{\text{Experimental degree of alkylation}}{\text{Maximum expected degree of alkylation}}\right) \quad (1)$$

the maximum expected degree of alkylation being calculated from the composition of the original mixture of chitosan and aldehyde.

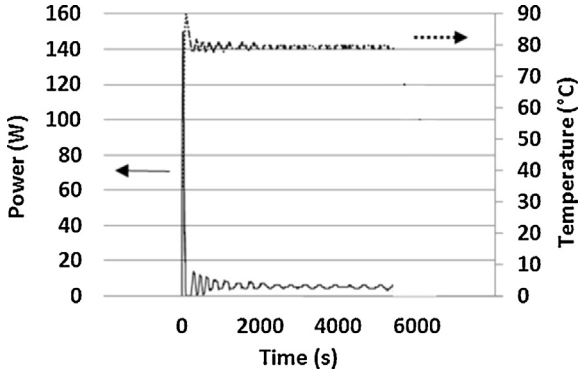


Fig. 1. Profiles of temperature and power: DYN mode (80 °C safe power: 150 W).

The irradiation fraction was defined as the fraction of the reaction time during which irradiation was performed.

The experimental conditions and characterization of alkylated chitosan samples are given in Table 1.

3. Results and discussion

3.1. Comparison between microwave irradiation modes

In order to be as reliable as possible, the irradiation mode was scrupulously studied to enhance the microwave irradiation during the polymer reaction. Pulsed power mode (SPS) and dynamic mode (DYN) are commonly used within the articles dealing with the microwave-assisted syntheses. The DYN mode is a temperature controlled mode with no constraint on the microwave irradiation power. On the other hand, SPS mode is temperature and power controlled, moreover, the vessel cavity is air-cooled throughout the reaction ensuring an optimized irradiation duration (Marcasuzaa et al., 2011). Within the present work, both modes have been compared and the results are reported in Figs. 1 and 2. This comparison has been conducted within the same experimental condition to be as reliable as possible: same vessel, same reaction volume and same microwave reactor. At last, acidic aqueous solution has been

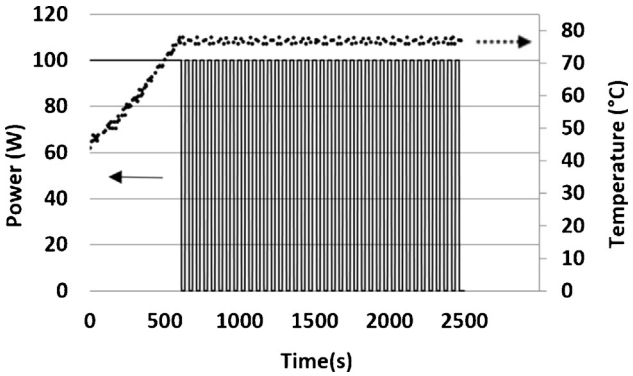


Fig. 2. Profiles of temperature and power: SPS mode (80 ± 1 °C, irradiation power: 100 W).

Table 1
Reaction conditions and characteristics of alkylated chitosans.[a]

Chitosan	Expected degree of alkylation	Reaction time (min)	Microwave yield of alkylation_(%irradiation)		Conventional yield of alkylation	
			25 °C	40 °C	25 °C	40 °C
Chi1	5%	60		100%_(54%)		
	10%	15		100%_(62%)		
		30		100%_(62%)		
		60	72%_(19%)	100%_(56%)	63%	91%
	20%	1		95%_(100%)	85%	
		3	81%_(71%)	95%_(73%)	84%	
		5	92%_(68%)			78%
		15				85%
		30				89%
		60		100%_(55%)		91%
Chi2	5%	60		100%_(59%)		
	10%	15		100%_(70%)		
		30		84%_(62%)		
		60	98%_(17%)	100%_(75%)	85%	64%
	20%	1	78%_(85%)	83%_(100%)		79%
		3	80%_(54%)	90%_(97%)	78%	86%
		5	81%_(45%)	92%_(67%)	74%	89%
		15	82%_(26%)	96%_(63%)	78%	91%
		30	83%_(16%)	97%_(60%)	78%	
		60	84%_(10%)	100%_(58%)	78%	

[a] The alkylated chitosan samples were prepared using SPS irradiation mode.

chosen for this experiment to be as close as possible from the target polymer reactions.

The monitoring of both the temperature and the irradiation power has been reporting within Fig. 1 for the DYN mode and Fig. 2 for the SPS mode. The temperature profiles of the polymerization were monitored using a calibrated infrared temperature control mounted beneath the reaction vessel. The reaction parameters (temperature, power, stirring, etc.) were set with a laptop and the SYNERGY software (version 1.35 from CEM Corp.). The records clearly showed that the DYN mode is defined by a high initial microwave power to reach the set reaction temperature (80 °C in Fig. 1) in less than dozens of seconds. As soon as the target temperature is reached, the microwave power decreased or was shut off completely to maintain it. As a result, most of the reaction is conducted with extremely low or no microwave irradiation. This behavior is even more pronounced in the case of this work because the reaction is conducted within polar solvent and ionic strength (Rigolini et al., 2009). On the other hand, SPS mode allows the control of the irradiation power along with a target reaction temperature. Moreover, the reaction is achieved under air cooling to cool down the reaction mixture and so overdo the microwave irradiation to maintain the target temperature with the set irradiation power. Within Fig. 2, the target temperature was 80 ± 2 °C and a set power of 100 W. This power value has been optimized by taking into account the polarity and the ionic strength of the reactive medium in order to irradiate the reaction medium as much as possible. The irradiation rate is defined as the ratio of the duration of the microwave irradiation versus the overall reaction time.

At last the temperature profile during a SPS procedure has been compared to that of a reaction conducted under conventional heating, i.e. within a water bath.

It is worth noticing that even at an irradiation power as low as 30 W, approximately 100 s are necessary under microwave irradiation (Fig. 3) to reach 40 °C while it takes almost 600 s in a pre-heated water bath to do the same. This feature reveals one of the advantage of using microwave assisted synthesis especially to reach quickly the desired temperature with a minimal amount of energy.

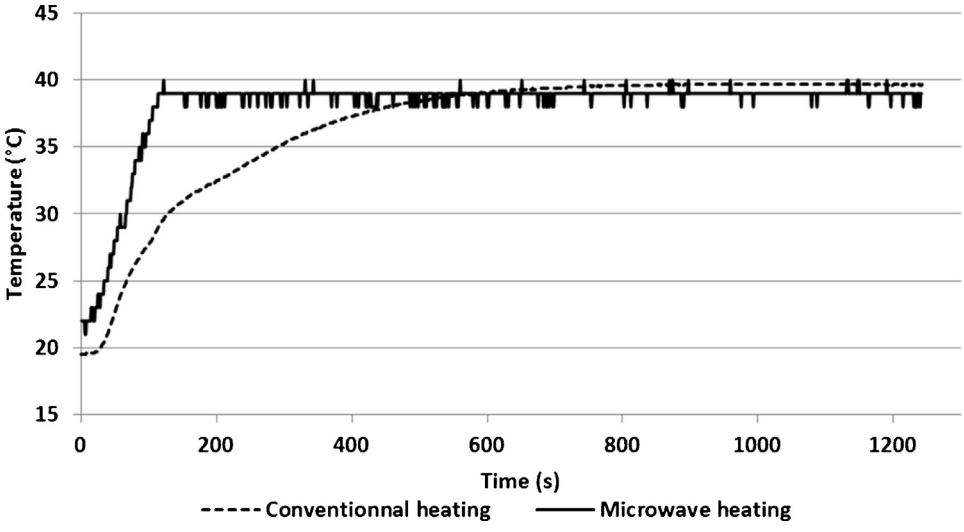


Fig. 3. Reactive medium temperature under microwave irradiation (SPS mode, $T = 40 \pm 1$°Cirradiation power 30 W) and conventional heating ($T = 40 \pm 1$°C).

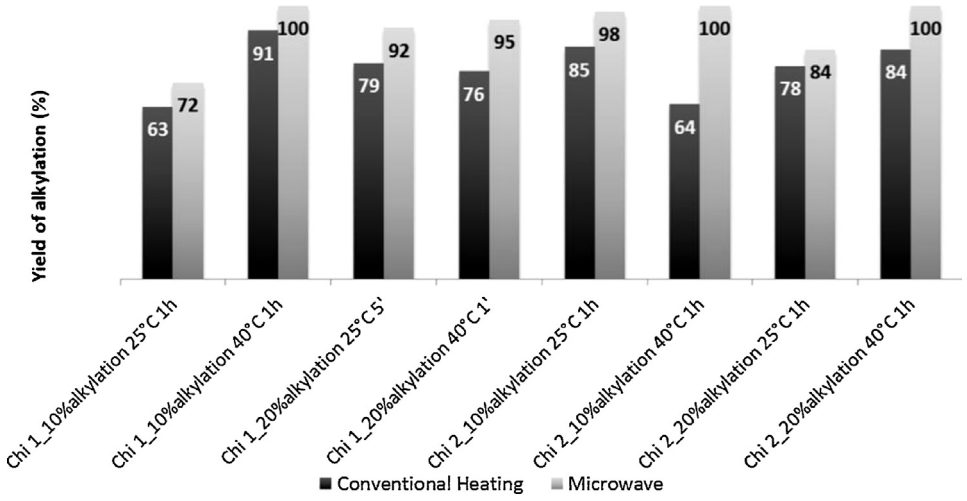


Fig. 4. Comparison of yields obtained in synthesis of alkylchitosan using conventional heating or microwave irradiation (SPS mode, irradiation power 30 W).

3.2. Reductive amination and role of reaction conditions

The greatest interest is to compare microwave irradiation and conventional heating in relation with alkylation of the chitosan chain (degree of alkylation as a function of reaction time). The most pertinent results are given in Fig. 4.

Whatever the chitosan sample, the target degree of alkylation and the temperature are, the yields obtained under microwave irradiation are larger than those obtained with conventional heating. It is worth noticing the sample related to the 10% alkylation of the larger molar mass chitosan: the microwave assisted reaction at 40 °C in one hour allows a 35% increase in the yield. When the different parameters (molar masses of chitosan, temperature and reaction duration) are considered it is observed from Table 1 that the molar mass has not a significant effect within the studied range (up to 200,000 g mol^{-1}).

Let us focus onto the 20% alkylated Chi2 under microwave irradiation (Fig. 5). This experiment highlights the role of different parameters on the efficiency of the reaction: the duration of the synthesis as well as the temperature, all of them being closely related to irradiation during the reaction.

Using a SPS microwave irradiation mode, the irradiation percentage is directly dependent on the reaction temperature if we consider the same set irradiation power. The higher the temperature is, the higher the irradiation rate is. As a consequence by considering the same reaction medium (in terms of reagents and volumes), the irradiation rate is higher at 40 °C than at 25 °C for a microwave power of 30 W. As a result, the increase of the reaction yield may be considered by taking in account both the temperature and the irradiation power.

The major effect of microwave irradiation occurs during the first minutes of the reaction allowing a sharp and controlled increase in temperature. When comparing a microwave-assisted and a conventional heating modification performed during the same duration, higher yields are obtained under irradiation. Microwaves allow reaching the target temperature in a shorter time (Fig. 5) and this feature explains the great yields obtained from the first minutes. From our knowledge, it is the first time that the kind of reaction has been done in such short time with quantitative yields. In other hand, these results also demonstrate that this reaction is endothermic.

Among the great impact of the microwaves toward the yields of the reaction, it was necessary to determine their effects on

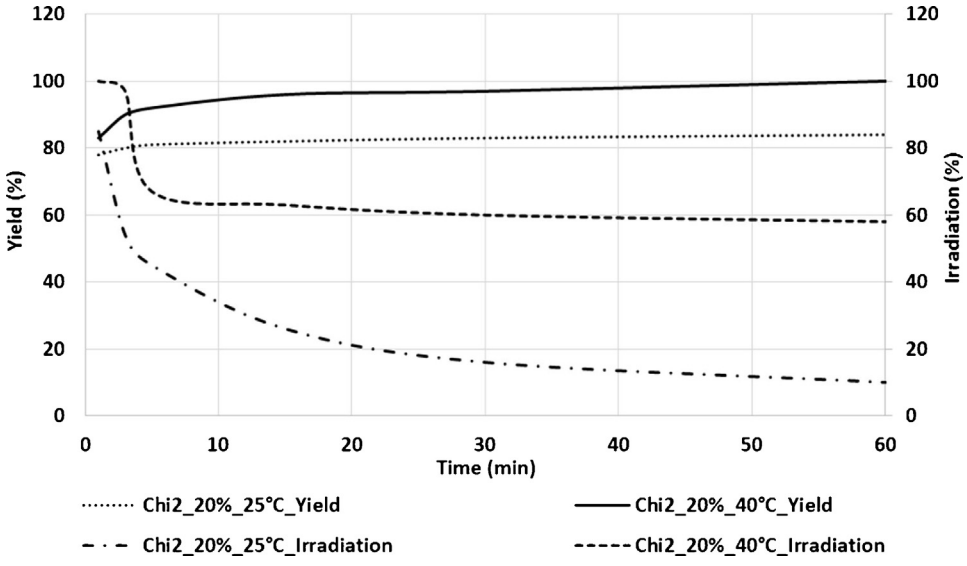


Fig. 5. Kinetics of alkylation of chitosan using SPS mode microwave irradiation ($T = 40 \pm 1$ °C, irradiation power 30 W, Chi2, expected degree of alkylation 20%).

the characteristics of the final product. The ^{1}H NMR spectroscopy demonstrates than no deacetylation occurs during this microwave assisted reaction (Supplementary information). Even though it is difficult to demonstrate using direct evidence that no chain degradation occurs during this reaction; many observations allow to assume such fact (Desbrieres et al., 1996). These results demonstrate, again, the interest of using microwave irradiation for such experiments increasing the yield of reaction without any modification of the macromolecular backbone while decreasing the energy used within the process.

As already mentioned, these amphiphilic natural polymers have interesting properties such as their ability to auto-associate (Desbrieres, 2004) and to improve interfacial properties of emulsions or foams (Desbrieres & Babak, 2006). The physico-chemical properties of such alkylated chitosans obtained using microwave irradiation have been studied and detailed below.

3.3. Properties of amphiphilic derivatives of chitosan

3.3.1. Rheology

Experiments were carried out at a concentration larger than the overlapping concentration c^* estimated from the relation $c^* \approx 1.2/[\eta]$ (Rotureau, Dellacherie, & Durand, 2006) to highlight any autoassociative behavior. Solutions of precursor chitosan have a Newtonian behavior while alkylchitosan solutions are rheothinning (Fig. 6).

When the viscosity values on the newtonian plateau (or at the lowest values of the shear rate) are compared or separately the intrinsic viscosities, a maximal value was observed at an alkylation degree of around 10% (Fig. 7). At low degree of alkylation, considering the low salt concentration and a polymer concentration higher than c^*, intermolecular interactions will be predominant and the viscosity increases. Then, higher number of hydrophobic alkyl chains reduces electrostatic repulsions and favors the intramolecular interactions leading to more compact chains as demonstrated by the decrease in the intrinsic viscosity.

The hydrodynamic diameters calculated from dynamic light scattering can be compared together and the same evolution as above was observed. This confirms the evolution of hydrophobic interactions in this system. This specific behavior was already observed by Rotureau et al. with amphiphilic derivatives of dextran (Rotureau, Chassenieux, Dellacherie, & Durand, 2005). They notice that as soon as the polysaccharide was modified with hydrophobic groups of sufficient length (C10), aggregates were formed in aqueous solution and their structure depends on the nature of the hydrophobic group and the degree of modification. A similar trend was observed with pullulan modified by cholesterol groups that are highly hydrophobic (Akiyoshi, Deguchi, Moriguchi, Yamaguchi, & Sunnamoto, 1993).

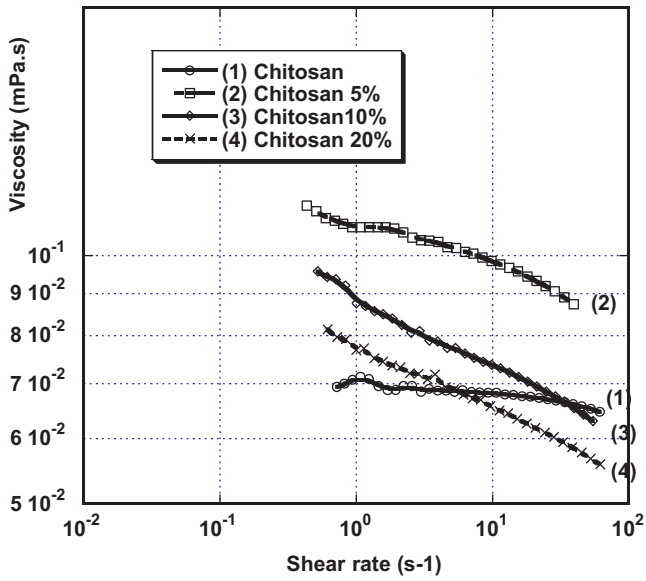


Fig. 6. Rheological behavior of chitosan and alkylated derivatives (Chi2, $c = 10\,g\,L^{-1}$, solvent: 0.2 M AcOH/0.05 M AcONa, microwave-assisted alkylation reaction under SPS mode, $T = 40 \pm 1°C$, $t = 60$ min).

3.3.2. Surface active properties

As expected, the surface tension experiments showed that precursor chitosan has no tensioactive properties. This corresponds to the known property of weakly hydrophobic polyelectrolytes to manifest poor adsorption activity at both oil–water and air–water interfaces, at relatively high degree of ionization (Babak, 1987). When alkyl chains were grafted onto the chitosan, the surface tension decreased demonstrating surface active properties for these amphiphilic polysaccharides as already discussed (Babak, Lukina, Vikhoreva, Desbrieres, & Rinaudo, 1999). The surface tension kinetics is quicker and quicker when the degree of alkylation and hydrophobicity increase. Moreover the surface tension values at equilibrium state seem to decrease when the degree of alkylation increases (Fig. 8).

These results showed that the alkylated chitosan obtained using the microwave-assisted process exhibits similar physico-chemical properties than derivatives prepared using conventional heating process.

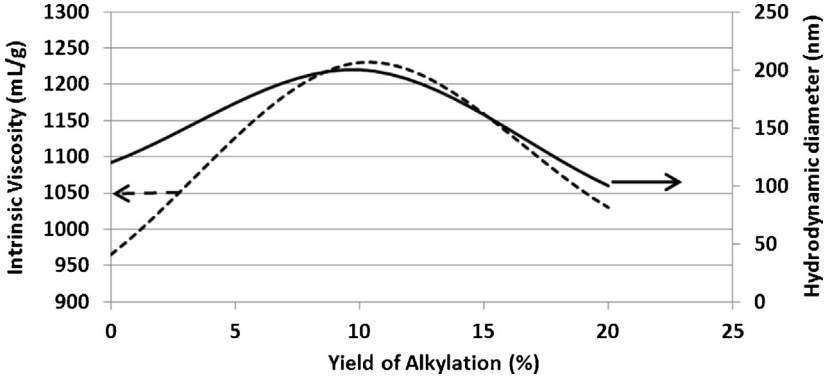


Fig. 7. Influence of degree of alkylation on intrinsic viscosity and hydrodynamic radius for alkylated Chi2 (solvent 0.3 M AcOH/0.05 M AcONa, microwave-assisted alkylation reaction under SPS mode, $T = 40 \pm 1°C$, $t = 60$ min).

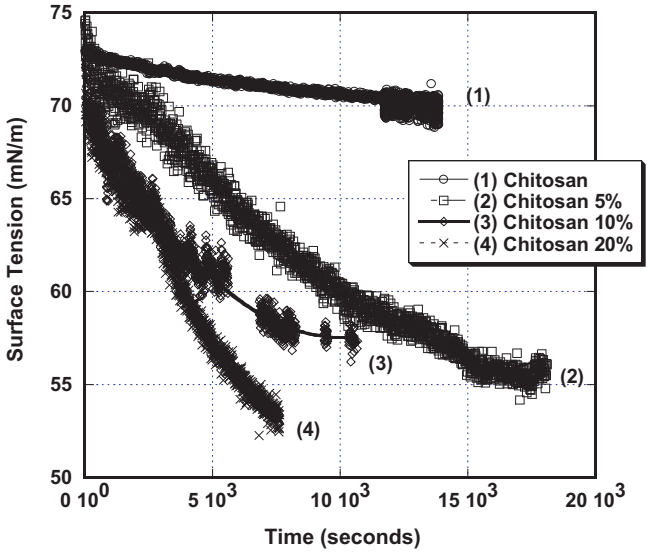


Fig. 8. Evolution of surface tension with time for alkylated Chi1 (solvent 0.2 M AcOH/0.05 M AcONa, microwave-assisted alkylation reaction under SPS mode, $T = 40 \pm 1^{\circ}C$, $t = 60$ min).

4. Conclusion

Within this work, microwaves have been successfully employed for the synthesis of amphiphilic derivatives of chitosan. When compared to modified chitosan obtained under conventional heating, the results showed that the irradiated chitosan exhibits the same properties in terms of viscosity and surface tension. Deeper characterization showed that microwaves did not affect the polymer backbone. At last but not least, the reaction is more efficient in terms of conversion under microwave irradiation and reaction times as low as few minutes have been optimized with quantitative yields. This is the first time that amphiphilic derivatives of chitosan have been obtained within such short time. By taken into account the ratio yield versus time, these results showed that it is possible to use microwave irradiation to go toward "green chemistry" considering energy aspects. Following the same strategy, further works will be dedicated to the grafting of conducting polymer (as poly(aniline)) onto chitosan and also on the synthesis of modified chitosan in solvent-free conditions.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.04.083.

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