



Novel cationic and amphiphilic pullulan derivatives II: pH dependant physicochemical properties

Z. Souguir^{a,b}, S. Roudesli^b, E. About-Jaudet^a, L. Picton^a, D. Le Cerf^{a,*}

^a University of Rouen, Laboratoire Polymères Biopolymères Surfaces, FRE 3101 & FR 3038 CNRS, 76821 Mont Saint Aignan, France

^b University of Monastir, Laboratoire des Polymères Biopolymères Matériaux Organiques, 5000 Monastir, Tunisia

ARTICLE INFO

Article history:

Received 11 May 2009

Received in revised form 9 September 2009

Accepted 2 November 2009

Available online 10 November 2009

Keywords:

Pullulan

Polysaccharide

Cationic

Amphiphilic

pH dependence

ABSTRACT

The physicochemical properties (viscosity, surface tension, zeta potential, size measurement) of Pullulan, DEAE-Pullulan ($DS_0 = 0.8$) (DS_0 is the degree of substitution of total nitrogen groups per anhydroglucose units (AGU)) and the alkylated derivatives Y- C_x -DEAE-Pullulan ($Y = 100 DS_{C_x}$ (DS_{C_x} : the number of alkyl groups per anhydroglucose units) Y is equal to 44 and 42 for C_{10} and C_{12} , respectively) were studied in aqueous salt-free solutions at pH 3, 8 and 11. For the DEAE-Pullulan a strong polyelectrolyte character at pH values below 8 was found, which, despite the presence of a sizeable fraction of permanent cationic charges due to a side chemical reaction (Hoffmann addition), evolved to a marked amphiphilic behavior in alkaline media. Alkylated DEAE-Pullulan derivatives (44% of C_{10} and 42% of C_{12}) are strongly amphiphilic regardless of the pH. The low intrinsic viscosity (Fuoss and Fedors models) values confirmed the degradation of cationic amphiphilic pullulan derivatives.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Cationic polymers have a vast array of applications. They are used in drug and gene delivery systems (San Juan, Hlawaty, Chaubet, Letourneur, & Feldman, 2007), as flocculants (Kostenbader & Cliver, 1972), as chromatography support (Jiulin & Dubin, 1994), and as bacterial and cellular adhesion modifier (Tribet & Vial, 2008). Most of them are quaternary ammonium polymers (Jiang, Wang, Yu, & Chen, 2005; Panarin, Solovskii, & Ékzemplyarov, 1971) and are not pH dependant. When the polymer presents ionizable weak basic moieties, the system is sensitive to pH variations (Chen, Wang, & Pelton, 2005). For example chitosan is soluble only in acidic media due to the ionization of amine groups (Rinaudo, Pavlov, & Desbrières, 1999). Formation of polycomplexes between polyanion and polycation is possible only if the two polyelectrolytes are ionized (Le Cerf, Simon, Argillier, & Picton, 2007).

Some cationic polymers show an amphiphilic character. Nichifor et al. have synthesized new polymers-hydrophobically modified cationic polysaccharides-based on dextran which bear pendant *N*-(2-hydroxypropyl)-*N,N*-dimethyl-*N*-alkylammonium chloride groups randomly distributed along the polymer backbone (Bai, Catita, Nichifor, & Bastos, 2007; Bai, Nichifor, Lopes, & Bastos, 2005; Nichifor, Lopes, Bastos, & Lopes, 2004). Extensive work is available on chitosan hydrophobically modified by reductive amination, leading to the grafting of hydrophobic alkyl chains along

the hydrophilic macromolecular chain (Desbrières, 2002; Ortona, D'Errico, Mangiapia, & Ciccarelli, 2008). The length of the alkyl chain and the degree of substitution of the amine function rate allow controlling the hydrophilic–lipophilic balance (HLB). These cationic and amphiphilic polymers can be used to form amphiphilic polycomplexes (Khutoryanskiy et al., 2003) able to solubilize hydrophobic compound or to modify surface properties.

The physicochemical properties of hydrophobically modified polysaccharides depend not only on the structural parameters of the polymer such as the nature of the macromolecular backbone, the length and the rate of hydrophobic moieties but also on environmental parameters (pH, salinity, temperature, etc.) (Chen et al., 2005; Sauer & Dee, 2002; Yaseen, Lu, Webster, & Penfold, 2005; Zhang & Marchant, 1996). The presence of amine and acid functions on the polysaccharide yields various pH which allows to modulate the physicochemical properties of the hydrophobically modified polysaccharide. Polyelectrolyte and hydrophobic characters of the polysaccharide are an additional difficulty in the physicochemical study. The presence of hydrophobic alkyl chains is generally accompanied by inter and/or intramolecular associations (Iliopoulos & Olsson, 1994; Magny, Iliopoulos, Zana, & Audebert, 1994) and formation of aggregates. The presence of electrostatic charges on the polysaccharide provides a polyelectrolyte effect (Blachford, 1969; Briggs, 1941; Rubio-Hernández, Carrique, & Ruiz-Reina, 2004). Several models are proposed for the determination of the intrinsic viscosity in free salt solution (Dragan & Ghimici, 2001; Fedors, 1979; Fuoss & Strauss, 1948; Korecz, Csacvari, & Tudos, 1988; Ng, Tam, & Jenkins, 1999).

* Corresponding author. Tel./fax: +33 2 35 14 65 43.

E-mail address: Didier.lecerf@univ-rouen.fr (D. Le Cerf).

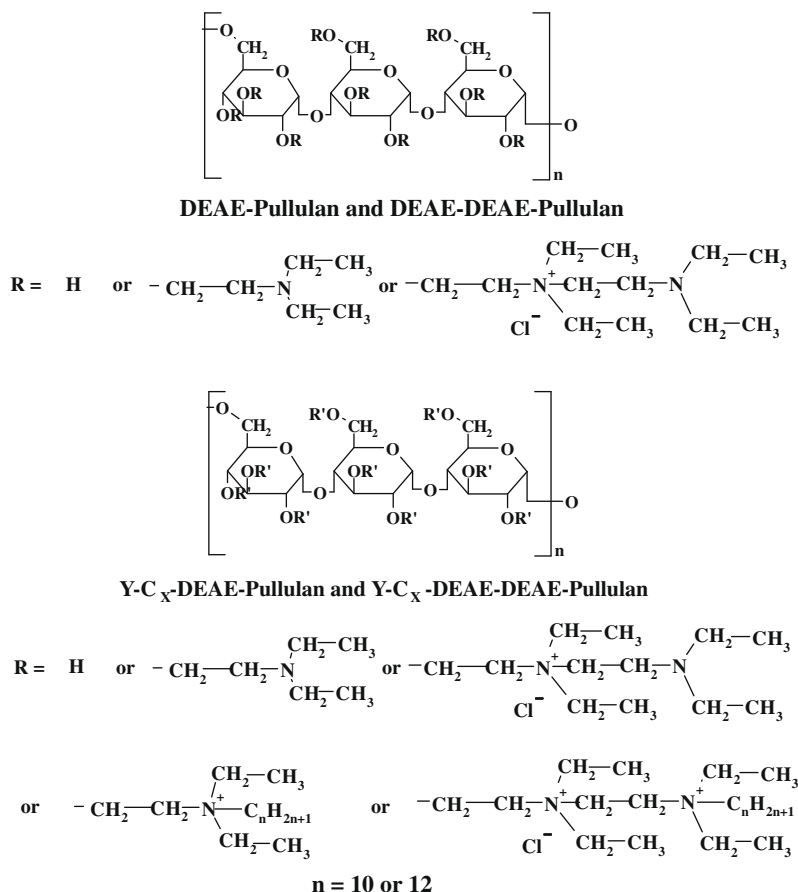


Fig. 1. Repeat unit of DEAE-Pullulan and alkyl DEAE-Pullulan derivatives.

Effectively we well know the Huggins equation (Huggins, 1942) applied for all neutral polymer or polyelectrolyte solution in ionic strength necessary to screen electrostatic repulsion. But the presence of electrostatic charges on the macromolecular backbone is traduced by the presence of polyelectrolyte effect in unentangled semi-dilute regime. The phenomena is observed when the reduce viscosity increase with the decrease of the polymer concentration. Generally the Fuoss equation (Fuoss & Strauss, 1948) is used to linearization of viscosimetric data in unentangled semi-dilute regime ($\eta \sim C_p^{1/2}$) (Rubinstein, Colby, & Dobrynin, 1994). The second model can be used is the Fedors equation used generally for moderate and dilute polyelectrolyte concentration (Fedors, 1979).

In a previous paper (Souguir, Roudesli, Picton, Le Cerf, & About-Jaudet, 2007), we have described the synthesis and the chemical characterization of diethylaminoethylpullulan (DEAE-Pullulan) and two of its hydrophobic derivates obtained by grafting decyl (44-C₁₀-DEAE-Pullulan) and dodecyl (42-C₁₂-DEAE-Pullulan) groups using Hoffmann alkylation reaction. For all the samples we have shown the coexistence of two functional types: an amine function at the end of DEAE group and a quaternary ammonium function when the DEAE group or alkyl group are linked to the DEAE group (Fig. 1). These macromolecules exhibit three kinds of charged groups with different pKa values. The tertiary amino group of the simple DEAE substituent has a pKa equal to 9.32 against 5.5 for the tertiary amino group of the tandem DEAE-DEAE substituent. All the quaternary ammonium groups have a pKa of 14 (Zobel et al., 1997). The two groups (tertiary amino and ammonium groups) are quantified by their degree of substitution (DS_N and DS_{N+}). By coupling flow field flow fractionation (F4) and multi an-

gle laser light scattering (MALLS) we have shown on the one hand that the polysaccharide is degraded by the Hoffman alkylation reaction, and on the other hand that intermolecular hydrophobic associations due to a major amphiphilic behavior in solution (0.1 mol L⁻¹ LiNO₃) were present.

In the present work we report the pH dependent behavior of these samples by zeta potential, hydrodynamic radius, surface tension and intrinsic viscosity measurements. The aim of combine of various physicochemical measurements in solution and at the interface is to obtain an overall picture of pullulan derivatives in salt free solution. In the work the strength ionic (C_s) is negligible in pH equal 3, 8 and 11 in comparison with polymer concentration.

2. Materials and methods

2.1. Materials

Pullulan is a linear and flexible polysaccharide produced by growing yeast-like fungi *Aureobasidium pullulans* on starch syrups. It was purchased from Hayashibara Biochemical Laboratory (Okoyama (Japan)). DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan were obtained by chemical modification of pullulan as reported in previous work (Souguir et al., 2007). For the alkylated derivatives the nomenclature used is Y-C_x-DEAE-Pullulan. Where Y is equal to 100 DS_{Cx} (DS_{Cx}: the number of alkyl groups per anhydroglucose units) and C_x is a number of carbon per alkyl chain. Their macromolecular characteristics are summarized in Table 1. The number and weight average molar masses of isolated

Table 1

Characteristics of pullulan, DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan (Souguir et al., 2007).

	M_n (g mol ⁻¹)	M_w (g mol ⁻¹)	DS_N	DS_{N+}
Pullulan	135,000	190,000	/	/
DEAE-Pullulan	250,000	333,000	0.65	0.15
44-C ₁₀ -DEAE-Pullulan	80,000	100,000	0.21	0.59
42-C ₁₂ -DEAE-Pullulan	84,000	100,000	0.23	0.57

chains were obtained by flow field flow fractionation (F4) coupled on line with angle laser light scattering (MALLS). The two substitution degrees DS_N (DS_N : the number of amine groups per anhydroglucose units) and DS_{N+} (the number of quaternary ammonium groups per anhydroglucose units determined by Eyler's equation ($DS_{N+} = DS_0 - DS_N$)) were obtained by conductimetric measurements, elemental analysis and ¹H NMR.

The pH was adjusted by adding HCl (1 mol L⁻¹) to obtain an acidic medium or by adding NaOH (1 mol L⁻¹) to obtain an alkaline medium.

2.2. Measurements methods

2.2.1. Surface tension measurements

The equilibrium surface tension of the aqueous solutions was measured according to the Wilhelmy plate method (Krüss K12 tensiometer, Germany). The platinum plate was cleaned before each measurement by immersion in deionised water followed by heating in a flame. The surface tension, γ (mN m⁻¹), was measured under controlled temperature ($T = 25^\circ\text{C}$) as a function of time. The equilibrium was obtained after 1 h.

2.2.2. Zeta potential measurements

Zeta potential measurements were carried out with a Zetasizer ZS (Malvern Instruments) at 25°C . The solutions were prepared in water, filtered through Millex 0.2 μm filter and poured in special cell (DTS 1060 disposable zeta cell, Malvern instruments). The zeta potential values were calculated with the DTS Dispersion Technology Software (Version 4.00 2003, Malvern instruments) using the Smoluchowski approximation (Egorova, 1994).

2.2.3. Size measurements

Particle size was measured using quasi elastic light scattering (QELS) with a Zetasizer ZS (Malvern Instruments) at 25°C . The mean hydrodynamic diameter (D_H) was calculated from the diffusion measurement using the Stokes–Einstein equation. The particle size was determined using Contn analysis mode.

2.2.4. Viscosity measurements

The viscosity measurements were performed using a Low Shear 30 (Contraves, Switzerland). All measurements were obtained in the Newtonian regime. The temperature around the Couette geometry was kept constant at 25°C thanks to the circulation of water from a controlled temperature bath. Viscosity data were analyzed using Huggins (1942), Fuoss and Strauss (1948), and Fedors (1979) relations, Eqs. (1)–(3), respectively,

$$\frac{\eta - \eta_0}{\eta_0 C_m} = \frac{\eta_{sp}}{C_p} = [\eta] + k_H [\eta]^2 C_p \quad (1)$$

$$\frac{C_p}{\eta_{sp}} = 1/[\eta] + B\sqrt{C_p} \quad (2)$$

$$\frac{1}{2(\sqrt{\eta_{rel}} - 1)} = \frac{1}{[\eta]} \times \left(\frac{1}{C_p} \frac{1}{C_m} \right) \quad (3)$$

where $[\eta]$ is intrinsic viscosity, B constant for Fuoss equation, η_{rel} relative viscosity, η apparent viscosity, η_0 apparent viscosity of water, k_H Huggins constant, η_{sp} specific viscosity, C_p polymer concentration and C_m concentration parameter for Fedors equation.

C_m is analogous to ϕ_m the maximum volume fraction to which solid spheres can pack in a suspension (Rotureau, Dellacherie, & Durand, 2006).

3. Results and discussion

The polymer derivatives are characterized by the presence of two functions: an amine function which is ionizable versus the pH, and a quaternary ammonium function, which is cationic and independent of the pH. The behavior of the pullulan derivatives is pH dependent due to the presence of the amine function. Measurements of the zeta potential, size variation, surface tension as well as the viscosimetric study were carried out at different pH.

Pullulan is a neutral hydrophilic polysaccharide that does not present hydrolytic degradation quickly in alkaline or acidic media.

3.1. Zeta potential

Fig. 2 shows the variation of the zeta potential versus pH (the lines are guides for the eyes) for DEAE-Pullulan and 44-C₁₀-DEAE-Pullulan. The two polymers present a similar behavior which corresponds to the overall decrease in the zeta potential when the pH increases. This is due to the progressive neutralization of the positive charges of the ammonium function from pH dependent amine groups. At pH 11, the zeta potential of 44-C₁₀-DEAE-Pullulan should be higher than that of DEAE-Pullulan because of a higher number of ammonium functions on 44-C₁₀-DEAE-Pullulan than on DEAE-Pullulan. However, two identical values were obtained for the two polymers. This anomaly can be explained by the presence of hydrophobic associations between the alkyl groups (aggregates). The presence of hydrophobic associations can hinder the cationic charges of alkylated derivatives.

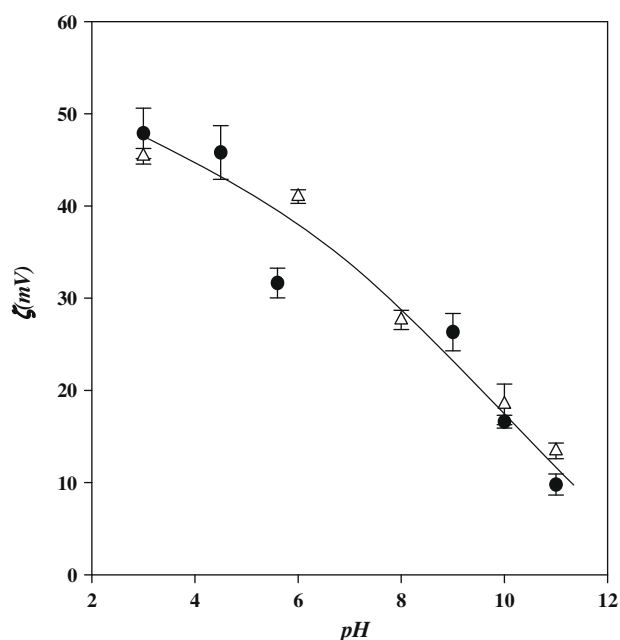


Fig. 2. Variation of zeta potential (ζ (mV)) versus pH for DEAE-Pullulan (●) and 44-C₁₀-DEAE-Pullulan (▲), $C_p = 0.5 \text{ g L}^{-1}$ at $T = 25^\circ\text{C}$.

3.2. Surface tension

Fig. 3 shows the curves representing the surface tension (the lines are guides for the eyes) of pullulan, DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan versus pH. The surface tension of pullulan is constant and the same as water (72 mN m⁻¹). Pullulan is a neutral hydrophilic polysaccharide that does not exhibit any surface activity at different pH. For the DEAE-Pullulan we observe a decrease of surface tension for pH above 8. This variation indicates a hydrophobic character which is due to the presence of ethyl groups after the neutralization of the ammonium function. The effect of alkylation on the adsorption of polymers to the water/air interface is very significant. For the two alkylated derivatives we observe a low surface tension at different pH due to the presence of the alkyl chains. At neutral pH, the values are comparable to published data on hydrophobically modified carbomethylpullulan (CMP). For example, at 1 g L⁻¹, 50 mN m⁻¹ for 35C8-CMP (Henni et al., 2005) and 43 mN m⁻¹ for 7C14-CMP (Henni-Silhadi et al., 2008). These data show that the surface-active properties of these hydrophobically modified polysaccharides are comparable. One of the advantages of grafting of alkyl groups on DEAE is the formation of quaternary ammonium functions. These functions increase the hydrophilic character of the polysaccharide backbone and allow the grafting of a higher quantity of hydrophobic groups.

An important result for the alkyl DEAE-Pullulan is its pH dependence. The decrease in surface tension in the basic medium is due to the neutralization of the ammonium function. This variation is less important than that observed for DEAE-Pullulan due to the difference in the number of ammonium functions on the alkylated derivative ($DS_N = 0.25$ and $DS_{N+} = 0.65$ for DEAE-Pullulan).

3.3. Hydrodynamic diameter measurement

Fig. 4 shows the variations of the hydrodynamic diameter (D_H (nm)) versus pH (the lines are guides for the eyes) for DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan. For DEAE-Pullulan, the values of the hydrodynamic diameter (D_H (nm)) are characteristic of isolated macromolecules (~1–100 nm). We observe a very significant decrease of the size when the pH increases. This result is

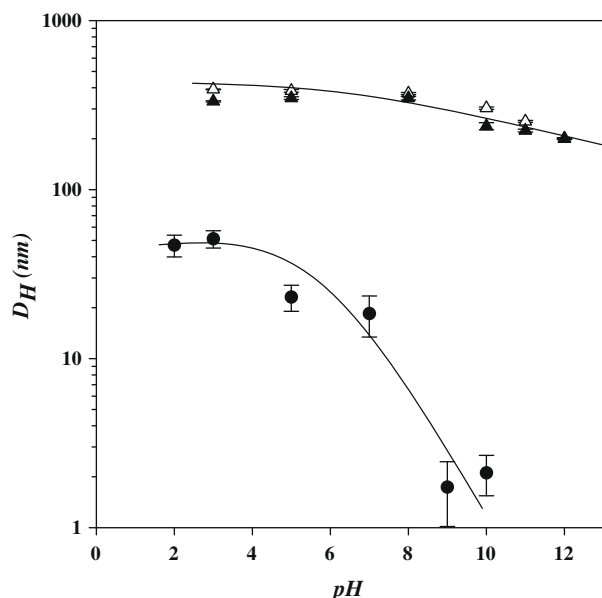


Fig. 3. Variation of surface tension (γ (mN m⁻¹)) versus pH in water for pullulan (○), DEAE-Pullulan (●), 44-C₁₀-DEAE-Pullulan (▲) and 42-C₁₂-DEAE-Pullulan (Δ), $C_p = 0.5$ g L⁻¹ at $T = 25$ °C.

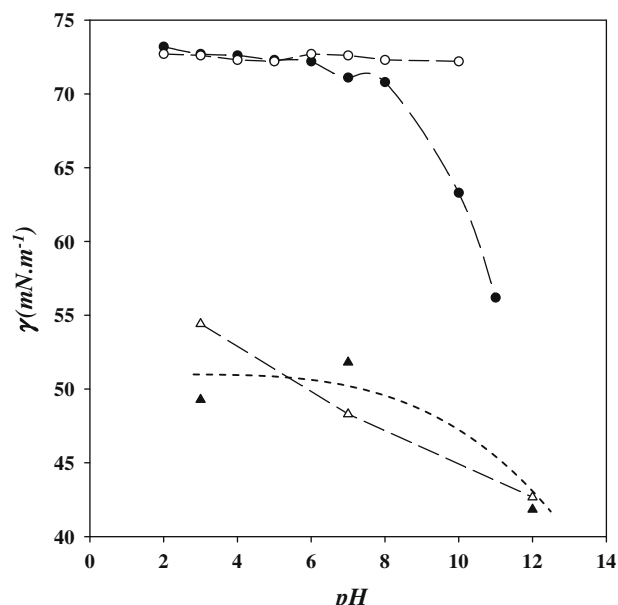


Fig. 4. Variation of hydrodynamic diameter (D_H (nm)) versus pH for DEAE-Pullulan (●), 44-C₁₀-DEAE-Pullulan (▲) and 42-C₁₂-DEAE-Pullulan (Δ) in water $C_p = 0.5$ g L⁻¹ at $T = 25$ °C.

due to the neutralization of the cationic functions (amine) which involve a disappearance of the electrostatic repulsions, and thus a reduction in the hydrodynamic volume. The presence of cationic permanent charge (ammonium function) in the basic pH seems insufficient to oppose intramolecular hydrophobic associations, which explains the decrease of the macromolecules size.

In the cases of the 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan, we observed higher sizes, although a high degradation as observed in F4/MALLS (Souguir et al., 2007) and a slight reduction in the D_H with the basic pH in comparison to DEAE-Pullulan were noted. We can deduce that, even in the presence of all the loads on the modified polysaccharide, part of the chains is self-associated by intermolecular hydrophobic associations (aggregates formation). Quasi elastic light scattering measurements are very sensitive to the presence of large particles (aggregates) even in very small quantity. In the case of the alkylated derivatives, the effect of the pH on the size of the aggregates is thus much less sensitive than on the isolated macromolecules.

3.4. Viscosity measurements

Fig. 5 shows the bilogarithmic variation of specific viscosity versus the concentration (Utraki Simha representation) for pullulan, DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan. The viscosity measurements for the four samples are obtained in pure water solution. The pH measured is equal to 8 for all samples.

For the pullulan solutions we observe two regimes of viscosity around a concentration near 20 g L⁻¹. The slopes (1.4 and 2.3) are characteristic of dilute and semi-dilute regimes for neutral polymers in water (the case of pullulan) or polyelectrolytes in high salt limit (Dou & Colby, 2008).

For the three other samples, which are under cationic form, we do not observe a concentration transition. The slope is lower (between 0.4 and 0.6). In this case, the polyelectrolyte solutions behave as a semi-dilute unentangled solution in low salt limit. Fuoss law can be used for analysis of viscometry data. The electrostatic blobs have self-avoiding walk conformation, and charge repulsion on larger scales simultaneously stretches the chain of electrostatic blocs locally. The distance between chains is quite close to the correlation length (Dou & Colby, 2008).

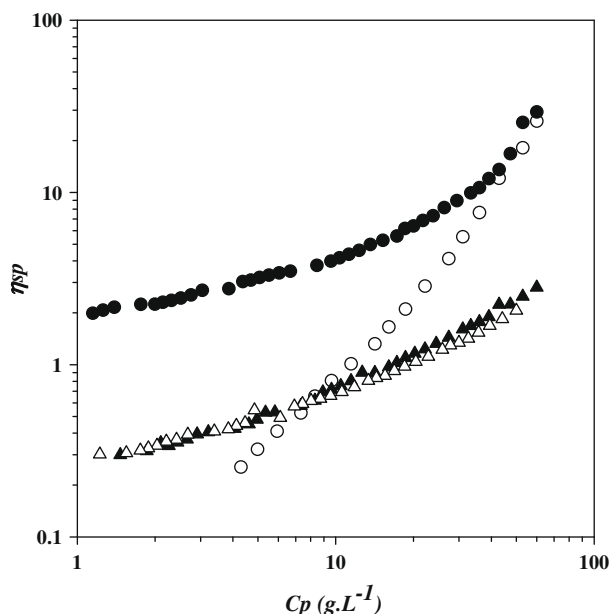


Fig. 5. Bilogarithmic variation of η_{sp} versus concentration in water for Pullulan (○), DEAE-Pullulan (●), 44-C₁₀-DEAE-Pullulan (▲) and 42-C₁₂-DEAE-Pullulan (Δ) at $T = 25^\circ\text{C}$.

Viscosities of 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan are lower than that of DEAE-Pullulan. This result can be explained by the degradation of the polymer during the synthesis of the

alkylated derivatives. A other explanation is the presence of intramolecular hydrophobic associations due to the alkyl groups.

Fig. 6 shows the variation of the reduced viscosity versus concentration for DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan at different pH. For the pullulan solutions (data not showed) the viscosity measurements versus pH give a similar behavior in different pH medium. Effectively, pullulan is a neutral polymer also the physicochemical properties are independent of pH. We observe a polyelectrolyte effect at pH 3 and 8 for the DEAE-Pullulan. For the solutions at pH 11 the reduced viscosity is constant and not dependent of concentration. At pH 3 and 8 the polymer is a polycationic and the repulsions between the cationic charges are very high at low concentration. In alkaline medium the ammonium functions are neutralized, thus explains the variation observed.

For the alkylated derivatives we observed a lower reduced viscosity than for DEAE-Pullulan in relation to the degradation during the synthesis. But at low concentration we note a polyelectrolyte effect at all pH. This is due to the higher quantity of quaternary ammonium functions.

Using these raw data we can determine the intrinsic viscosities using Huggins models (without polyelectrolyte effect) and using Fuoss and Fedors models (with or without polyelectrolyte effect). The obtained intrinsic viscosities are summarized in Table 2 in which we added the data for the pullulan precursor (neutral polysaccharide).

For pullulan, the intrinsic viscosity is constant for all pH as pullulan is a neutral polymer. The intrinsic viscosity of DEAE-Pullulan is higher than that of the pullulan precursor. That difference is

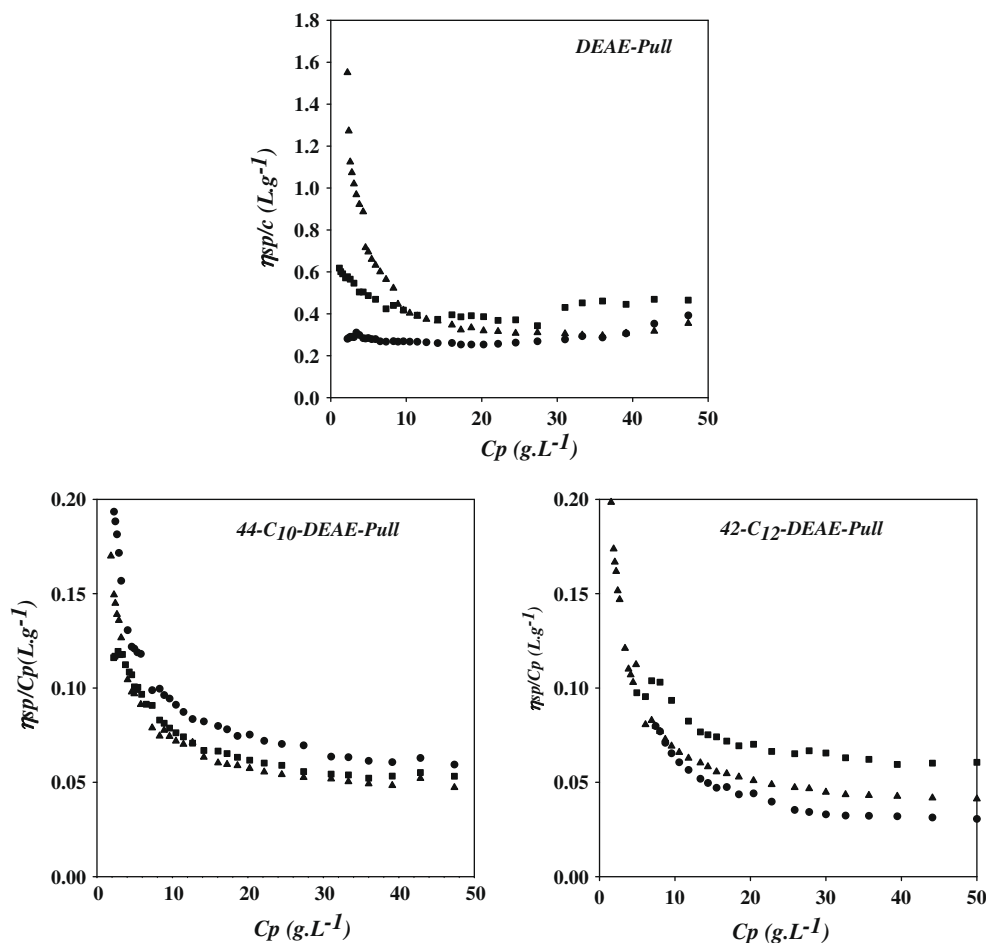


Fig. 6. Variation of η_{sp}/C_p versus concentration in water for DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan in pH 3 (■), pH 8 (▲) and pH 11 (●) at $T = 25^\circ\text{C}$.

Table 2

Value of intrinsic viscosity ($[\eta]$ (L g⁻¹)) for pullulan, DEAE-Pullulan, 44-C₁₀-DEAE-Pullulan and 42-C₁₂-DEAE-Pullulan in water obtained by Huggins, Fuoss, and Fedors models at pH 3, 8 and 11 at T = 25 °C.

	pH	$[\eta]_{\text{Huggins}}$ (L g ⁻¹)	$[\eta]_{\text{Fuoss}}$ (L g ⁻¹)	$[\eta]_{\text{Fedors}}$ (L g ⁻¹)
Pullulan	/	0.06	0.05	0.05
DEAE-Pullulan	3	/	2.0	1.8
	8	/	1.6	1.8
	11	0.25	0.29	0.25
44-C ₁₀ -DEAE-Pullulan	3	/	0.26	0.22
	8	/	0.25	0.22
	11	/	0.20	0.25
42-C ₁₂ -DEAE-Pullulan	3	/	0.25	0.22
	8	/	0.25	0.20
	11	/	0.06	0.06

due to the intra and intermolecular electrostatic repulsions of the quaternary ammonium function (polyelectrolyte effect). The variation of intrinsic viscosity with pH is similar than that observed in the size measurements. The neutralization of the ammonium function decreases the electrostatic repulsion, which decreases the hydrodynamic volume, thus decreasing the intrinsic viscosity.

For the alkylated derivatives we obtain similar intrinsic viscosity regardless of the model used. The viscosity is lower than that of DEAE-Pullulan, which is probably due to degradation as observed with flow field flow fractionation, but higher than that of pullulan. That difference can be explained by the presence of aggregates due to intermolecular hydrophobic associations. We observe a low sensitivity towards pH due to the low quantity of amine functions in these derivatives. In the case we can observe a difference between macroscopic and microscopic measurements techniques, the intrinsic viscosity is proportional to the hydrodynamic diameter (Stokes–Einstein relation) but in the case of alkylated derivatives the intrinsic viscosity is lower than of DEAE-Pullulan where the hydrodynamic diameter of this is lower than alkylated derivatives. The result confirms the great sensibility of light scattering in presence of object with very high hydrodynamic diameter in very low concentration.

4. Conclusion

In this paper we have shown the pH dependent behavior of DEAE-Pullulan and alkylated DEAE-Pullulan derivatives.

In the case of DEAE-Pullulan, a polyelectrolyte effect at pH values below 8 and a surfactant character in basic medium were obtained. These features are due to the neutralization of modulated ammonium functions and to the presence of diethyl groups. Measurements of the hydrodynamic diameter showed that the macromolecular chains were isolated.

In the case of the alkylated derivatives, we observed a high amphiphilic character. However, the size measurements indicated the presence of aggregates due to intermolecular associations. A low variation of the physicochemical properties versus pH was observed for the alkylated derivatives.

Acknowledgments

The authors want to thanks the 'Institut Français de Coopération en Tunisie' for their financial support. The authors are particularly grateful to Dr. Guy Muller and Dr. Anne Laurence Dupont for very helpful discussions.

References

Bai, G., Nichifor, M., Lopes, A., & Bastos, M. (2005). Thermodynamics of self-assembling of hydrophobically modified cationic polysaccharides and their

mixtures with oppositely charged surfactants in aqueous solution. *Journal of Physical Chemistry B*, 109(46), 21681–21689.

Bai, G., Catita, J., Nichifor, M., & Bastos, M. (2007). Microcalorimetric evidence of hydrophobic interactions between hydrophobically modified cationic polysaccharides and surfactants of the same charge. *Langmuir*, 13(12), 3119–3123.

Blachford, J. (1969). Theory of the secondary electroviscous effect for nonidentical particles. *Journal of Physical Chemistry*, 73(10), 3512–3513.

Briggs, D. R. (1941). Studies in electrokinetics. XXIV. The electroviscous effect. I. In systems of sodium gum Arabic. *Journal of Physical Chemistry*, 45(5), 866–876.

Chen, X., Wang, Y., & Pelton, R. (2005). PH-dependence of the properties of hydrophobically modified polyvinylamine. *Langmuir*, 21(25), 11673–11677.

Desbrières, J. (2002). Physico-chemical properties of chitosan and its hydrophobic derivatives. In R. A. Muzzarelli & C. Muzzarelli (Eds.), *Chitosan in pharmacy and chemistry* (pp. 429–435). Italy: Atec.

Dou, S., & Colby, R. H. (2008). Solution rheology of a strongly charged polyelectrolyte in good solvent. *Macromolecules*, 41(17), 6505–6510.

Dragan, S., & Ghimici, L. (2001). Viscometric behaviour of some hydrophobically modified cationic polyelectrolytes. *Polymer*, 42(7), 2887–2891.

Egorova, E. M. (1994). The validity of the Smoluchowski equation in electrophoretic studies of lipid membranes. *Electrophoresis*, 15(1), 1125–1131.

Fedors, R. F. (1979). An equation suitable for describing the viscosity of dilute to moderately concentrated polymer solutions. *Polymer*, 20(2), 225–228.

Fuoss, R. M., & Strauss, U. P. (1948). Polyelectrolytes. II. Poly-4-vinylpyridonium chloride and poly-4-vinyl-N-butylpyridonium bromide. *Journal of Polymer Science*, 3(2), 246–263.

Henni, W., Deyme, M., Stchakovsky, M., Le Cerf, D., Picton, L., & Rosilio, V. (2005). Aggregation of hydrophobically modified polysaccharides, in solution and at the air–water interface. *Journal of Colloid and Interface Science*, 281(2), 316–324.

Henni-Silhad, W., Deyme, M., Ruiz de Hoyos, M., Le Cerf, D., Picton, L., & Rosilio, V. (2008). Influence of alkyl chains length on the conformation and solubilization properties of amphiphilic carboxymethylpullulans. *Colloid and Polymer Science*, 286, 1299–1305.

Huggins, M. L. (1942). The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. *Journal of American Chemical Society*, 64(11), 2716–2718.

Iliopoulos, I., & Olsson, U. (1994). Polyelectrolyte association to micelles and bilayers. *Journal of Physical Chemistry*, 98(5), 1500–1505.

Jiang, S., Wang, L., Yu, H., & Chen, Y. (2005). Preparation of crosslinked polystyrenes with quaternary ammonium and their antibacterial behavior. *Reactive & Functional Polymers*, 62(2), 209–213.

Jiulin, X., & Dubin, P. L. (1994). Chromatographic evaluation of the binding of lysozyme to poly(dimethyldiallylammonium chloride). *Journal of Chromatography*, 667(1–2), 311–315.

Khutornyanskiy, V. V., Nurkeeva, Z. S., Mun, G. A., Sergaziyev, A. D., Ryskalieva, Z., & Rosiak, J. M. (2003). Polyelectrolyte complexes of soluble poly-2 [(methacryloyloxy)ethyl] trimethylammonium chloride and its hydrogels with poly(acrylic acid). *European Polymer Journal*, 39(4), 761–766.

Korecz, L., Csacvari, E., & Tudos, F. (1988). Physical chemistry of polyelectrolytes. *Polymer Bulletin (Heidelberg, Germany)*, 19(5), 493–500.

Kostenbader, K. D., Jr., & Cliver, D. O. (1972). Polyelectrolyte flocculation as an aid to recovery of enteroviruses from oysters. *Applied Microbiology and Biotechnology*, 24(4), 540–543.

Le Cerf, D., Simon, S., Argillier, J. F., & Picton, L. (2007). Contribution of flow field flow fractionation with on line static and dynamic light scattering to the study of hydrosoluble polyelectrolyte complexes. *Analytica Chimica Acta*, 604, 2–8.

Magny, B., Iliopoulos, I., Zana, R., & Audebert, R. (1994). Mixed micelles formed by cationic surfactants and anionic hydrophobically modified polyelectrolytes. *Langmuir*, 10(9), 3180–3187.

Ng, W. K., Tam, K. C., & Jenkins, R. D. (1999). Evaluation of intrinsic viscosity measurements of hydrophobically modified polyelectrolyte solutions. *European Polymer Journal*, 35(7), 1245–1252.

Nichifor, M., Lopes, S., Bastos, M., & Lopes, A. (2004). Self-aggregation of amphiphilic cationic polyelectrolytes based on polysaccharides. *Journal of Physical Chemistry B*, 108(42), 16463–16472.

Ortona, O., D'Errico, G., Mangiapia, G., & Ciccirelli, D. (2008). The aggregative behavior of hydrophobically modified chitosans with high substitution degree in aqueous solution. *Carbohydrate Polymers*, 74(1), 16–22.

Panarin, E. F., Solovskii, M. V., & Ékzemlyarov, O. N. (1971). Synthesis and antimicrobial properties of polymers containing quaternary ammonium groups. *Pharmaceutical Chemistry Journal*, 5(7), 24–26.

Rinaudo, M., Pavlov, G., & Desbrières, J. (1999). Solubilization of chitosan in strong acid medium. *International Journal of Polymer Analytical Characterization*, 5, 267–276.

Rotureau, E., Dellacherie, E., & Durand, A. (2006). Viscosity of aqueous solutions of polysaccharides and hydrophobically modified polysaccharides: Application of Fedors equation. *European Polymer Journal*, 42, 1086–1092.

Rubinstein, M., Colby, R. H., & Dobrynin, A. V. (1994). Dynamics of semidilute polyelectrolyte solutions. *Physical Review Letters*, 73(20), 2776–2779.

Rubio-Hernández, F. J., Carrique, F., & Ruiz-Reina, E. (2004). The primary electroviscous effect in colloidal suspensions. *Advance in Colloid and Interface Science*, 107(1), 51–60.

San Juan, A., Hlawaty, H., Chaubet, F., Letourneur, D., & Feldman, L. J. (2007). Cationized pullulan 3D matrices as new materials for gene transfer. *Journal of Biomedical Materials Research A*, 82A(2), 354–362.

- Sauer, B. B., & Dee, G. T. (2002). Surface tension and melt cohesive energy density of polymer melts including high melting and high glass transition polymers. *Macromolecules*, 35(18), 7024–7030.
- Souguir, Z., Roudesli, S., Picton, L., Le Cerf, D., & About-Jaudet, E. (2007). Novel cationic and amphiphilic pullulan derivatives I: Synthesis and characterization. *European Polymer Journal*, 43(12), 4940–4950.
- Tribet, C., & Vial, F. (2008). Flexible macromolecules attached to lipid bilayers: Impact on fluidity, curvature, permeability and stability of the membranes. *Soft Matter*, 4, 68–81.
- Yaseen, M., Lu, J. R., Webster, J. R. P., & Penfold, J. (2005). Adsorption of single chain zwitterionic phosphocholine surfactants: Effects of length of alkyl chain and head group linker. *Biophysical Chemistry*, 117(3), 263–273.
- Zhang, T., & Marchant, R. E. (1996). Novel polysaccharide surfactants: The effect of hydrophobic and hydrophilic chain length on surface active properties. *Journal of Colloid and Interface Science*, 177(2), 419–426.
- Zobel, H. P., Kreuter, J., Werner, D., Noe, C. R., Kümel, G., & Zimmer, A. (1997). Cationic polyhexacyanoacrylate nanoparticles as carriers for antisense oligonucleotides. *Antisense Nucleic Acid Drug Development*, 7, 483–493.