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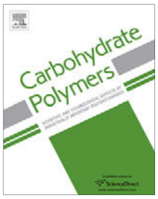

Unusual rheological properties of a new associative polysaccharide in salt media

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ABSTRACT

New amphiphilic polysaccharides based on alginate-grafted-Poly (ε-caprolactone) or alg-g-PCL bearing two kinds of PCL chains with different molar masses (1250 and 530 gmol^{-1}) with various amounts from 3% to 15% were prepared. Rheological properties in aqueous solutions of such systems have been investigated as a function of polymer concentration, added salt and temperature in semi-dilute regime. Strong hydrophobic intermolecular associations were clearly demonstrated in pure water whatever the PCL chain length and extend of modification. Increasing polymer concentration, grafting rate and/or PCL chains length can lead to a structured liquid behaviour. Rheological properties of the most organized system have been found independent to the temperature (until 60 °C). In salt media, a strong dependence of hydrophobic interactions to the length of PCL chains was observed. For M_{PCL} = 1250 g.mol^{-1} the screening of charges promotes the establishment of intermolecular interactions and leads to a strong physical gel for the highest grafting rates. For M_{PCL} = 530 g mol^{-1}, ionic strength leads to a decrease of rheological properties when increasing grafting rate. This result may indicate an increase of hydrophobic clusters even in the entangled regime. This unusual behaviour opens the ways for the preparation of suitable hydrogels for drug release.

1. Introduction

The transport of hydrophobic molecules in aqueous media has become an attractive field since the last two decades and applications are of potential interest for pharmaceutics, biomedical or biotechnology. One solution consists in using matrices made of hydrophilic polymers, notably from natural origin as polysaccharides suitable for biocompatibility, which are able to evidence hydrophobic clusters, (Akiyoshi & Sunamoto, 1996; Henni-Silhadi et al., 2008; Leonard, Rastello De Boisseson, Hubert, Dalençon, & Dellacherie, 2004; Mocanu, Mihaï, Le Cerf, Picton, & Muller, 2003; Mocanu, Mihaï, Picton, Le Cerf, & Muller, 2002; Noble, Gray, Sadiq, & Uchegbu, 1999). Over the last three decades, water-soluble amphiphilic polysaccharides have been extensively studied, due to their associative properties in solution (Desbrieres, 2004; Desbrieres, Martinez, & Rinaudo, 1996; Duval, Le Cerf, Picton, & Muller, 2001; Fisher et al., 1998; Sinquin, Hubert, Marchal, Choplin, & Dellacherie, 1996). This type of polymer in aqueous solution, leads to physical interactions among the hydrophobic groups, which can result in strong intra or intermolecular associations. The transition between intra and intermolecular association depends on many intrinsic (molar mass, rigidity of the backbone, nature and amount of hydrophobic moieties, neutral or charged…) and extrinsic (pH, ionic strength, temperature…) factors. This transition is mainly due to the polymer concentration (Rotureau, Dellacherie, & Durand, 2005; Simon, Dugast, Le Cerf, Picton, & Muller, 2003). For polyelectrolytes, ionic strength becomes a crucial parameter which is well known to enhance the association by screening electrostatic repulsion (Souguir, Roudesli, About-Jaudet, Le Cerf, & Picton, 2007; Wang, Ilopoulos, & Audebert, 1988). At low polymer concentration, intramolecular associations often prevail and when the concentration increases, intermolecular associations are classically favoured leading to the formation of superstructures, yielding a physical network that enhances the viscosity of an aqueous formulation. Consequently they are often used, in semi-dilute regime, as thickening agents or efficient rheology modifiers (Tsitsilianis & Iliopoulos, 2002; Winnik & Yekta, 1997) in many fields of applications such as paints, cosmetics, foods and oil recovery (Ng, Tam, & Jenkins, 2001; Semenov & Rubinstein, 2002).

On the contrary, some amphiphilic polyelectrolytes in aqueous solution evidence low viscosity up to high polymer contents. Such behaviour of so-called polysoaps is considered to be a key feature distinguishing ionic polysoaps from ordinary polyelectrolytes. In this case, low viscosities are explained by intramolecular aggregation of an important number of hydrophobic side chains, keeping the hydrodynamic radius small (Laschewsky, 1995). Since the pioneering works of Strauss in the 50th, these peculiar polymers have been extensively studied from both experimental (Bezzaoucha et

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al., 2007; Laschewsky, 1995) and theoretical point of view (Borisov & Halperin, 1995, 1999). Polysoaps may give rise to highly collapsed conformation (pseudo-micelle) by analogy with the micelles obtained with simple molecular surfactant. In the case of associative polysaccharides the term of polysoap is not usually employed as such systems often bear few long alkyl side chain and generally develop thickening rheological properties in the semi-dilute regime due to the sticky reptation of entangled chains (Leibler, Rubinstein, & Colby, 1991).

In a recent study, Henni-Silhadi et al. (2007) have clearly demonstrated that the solubility of an amphiphilic drug is greatly enhanced in an associative polysaccharide system which presents in dilute solution mainly intramolecular associations. Elsewhere, the elaboration of polymer matrices or hydrogels (physically or chemically crosslinked) for hydrophobic drugs controlled release, needs highly entangled solutions of polymer. It is also well established that in the case of 'associative polymer', intermolecular associations mainly prevail in the semi-dilute concentration regime. Thus, it seems challenging to obtain a system based on hydrophobically modified polymer conjugating both highly sticky-entangled solution and well structured hydrophobic clusters. The suitable candidate should be an amphiphilic polysaccharide showing properties between an associative thickener and polysoap.

In a previous study (Colinet, Dulong, Hamaide, Le Cerf, and Picton, 2009), we have described the preparation, by new aqueous micellar grafting technique, of original water-soluble and amphiphilic alginate grafted with poly(ε-caprolactone) (Alg-g-PCL) with two different molar masses of PCL (530 and 1250 g mol^{-1}) and molar hydrophobe contents from 3.5% to 15% (elementary analysis). By means of Flow Field Flow Fractionation (F4)/MALLS and/or viscometric measurements, the expected associative behaviour has been shown in pure water (both dilute and semi-dilute regimes) whatever the length of the PCL chains (Fig. 1a and c). Thanks to intermolecular hydrophobic associations, viscosities of such systems are substantially increased with polymer concentration and length or amount of PCL side chain (Rotureau et al., 2005; Selb, Volpert, & Candau, 1997; Simon et al., 2003, Sinquin et al., 1996). Usually such associative polyelectrolytes gives rise to an enhancement of intermolecular association (i.e. viscosity enhancement) when electrostatic repulsions are screened by added salt (Wang et al., 1988). That has been effectively observed for the alg-g-1250 samples (Fig. 1b). On the contrary, alginate grafted with various amount of 530 g mol^{-1} PCL chains evidence a much more limited increase in viscosity with increasing polymer concentration for higher amount of PCL (Fig. 1d). For these samples, it seems that intramolecular hydrophobic interactions or 'local collapse' still remain, even in semi-dilute regime. This 'polysoaps' like behaviour (non-classical for such associative polyelectrolyte) may open the way for the conception of amphiphilic matrices with hydrophobic clusters for controlled release applications. In the present paper, we report the rheological properties of these systems. This will allow our previous results in a more concentrated regime to be confirmed. Effectively, we need entangled conditions to elaborate the amphiphilic hydrogels using the well-known alginate-calcium method (Rousseau, Le Cerf, Picton, Argillier, & Muller, 2004).

2. Materials and methods

2.1. Materials

Sodium alginate of number and mass average molar mass $\overline{Mn}$ and $\overline{Mw}$ of about 195,000 and 350,000 g mol^{-1}, respectively (determined from SEC/MALLS measurements, Rousseau et al., 2004) and with a ratio $M/G = 0.5$ was purchased from Degussa company. Unfortunately we did not have information on M and G

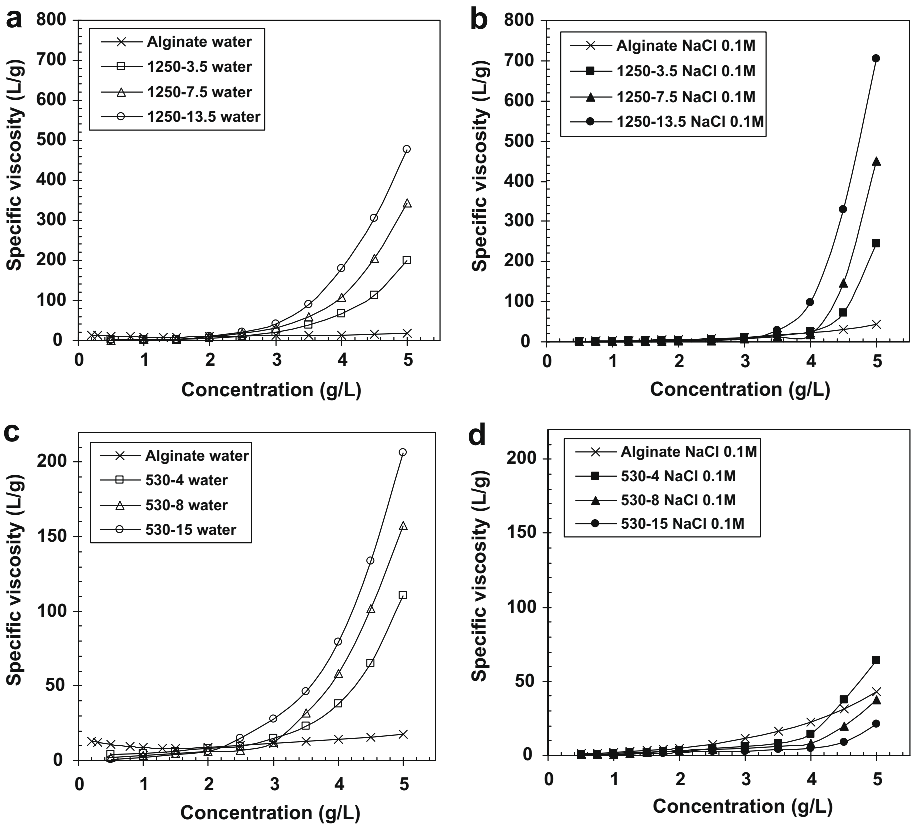


Fig. 1. Specific viscosity versus polymer concentration for alginate and alginate-g-PCL in water and NaCl 0.1 M at 25 °C (from Colinet et al., 2009).

block lengths and distribution. These factors should be of primary importance mainly as concerns the rheological properties (Morch, Donati, Strand, & Skjak-Braek, 2007). A complete description of the synthesis methodology of the alg-g-PCL has been previously reported (Colinet et al., 2009). Briefly, these derivatives have been prepared by an aqueous micellar grafting technique from alginate and poly(ε-caprolactone). The structure of these copolymers consists of a main polysaccharidic backbone (alginate) substituted by grafts of PCL via ester links. Amphiphilic copolymers were synthesized with two different molar masses of PCL (530 and 1250 g mol^{-1}). Molar hydrophobe contents (i.e. PCL chain determined by elementary analysis) ranged from 3.5% to 15% with respect to the uronic acid units. Modified alginates are coded as following: Molar mass of the grafted PCL – real incorporating rate (x). As example 1250-13.5 means an alginate-g-PCL with 13.5% of 1250 g mol^{-1} PCL. Water was purified with the Milli-Q reagent system (Millipore).

2.2. Summary of our previous results

Table 1 appears as an abstract of the previously obtained results. The reported molar masses ($\overline{\mathrm{Mn}}$) indicate that no degradation occurs during the modification of alginate. Moreover, it is evidenced (mainly with $\overline{\mathrm{Mw}}$ and Rh values) that a strong aggregation occurs which is enhanced with both amount and length of PCL. In dilute regime, intramolecular associations are clearly effective as showed by the values of intrinsic viscosities which are always much lower for hydrophobically modified samples than for the alginate precursor. Polymer associations are also apparent from the values of the Huggins coefficient. Thanks to Utracki & Simha representation (Utracki & Simha, 1963), the critical concentrations (Ccr) between dilute and semi-dilute regime have been determined in water and in the presence of salt. Whatever the media, these Ccr are always lower for modified alginate than for the precursor. For modified samples, it appears that upper 5 g L^{-1} we reach the semi-dilute range of concentration. For amphiphilic hydrosoluble polymers, Ccr indicates both the spatial occupation of macromolecular chains and their connectivity due to intermolecular associations (Simon et al., 2003). For alg-g-1250, the transition occurs logically for lower concentration when amount of grafted PCL increases. The contrary is observed for alg-g-530. This result may indicate that the connectivity (i.e. intermolecular associations) is more difficult for 530-*x* than for 1250-*x*. Alginate grafted with the lower PCL length (i.e. 530 g mol^{-1}) may have the properties of both a polysoap and a thickener.

2.3. Rheological measurements

Flow and oscillatory measurements were performed using a controlled stress rheometer AR 2000 (TA instrument) with a Peltier temperature control device. All the measurements were performed with a solvent trap to prevent any evaporation of the solvent. The storage (G') and loss (G'') moduli were measured as a function of frequency at the desired temperature (often 25 °C) under low applied stress (σ), in the linear viscoelasticity domain where no rupture of intermolecular associations occurs. The linearity of viscoelastic properties was carefully checked for all the investigated solutions before the measurements of G' and G'' moduli. Two types of measuring geometries were used: a cone with diameter of 40 mm and angle of 2° for viscoelastic solutions of alg-g-PCL, and plate geometry for solutions with a mainly elastic behaviour. Temperature ramps from 20 to 60 °C were applied at a rate of 2 °C/min using a Peltier plate. Polymer solutions were prepared by dissolving the solid polymer in milli-Q water under vigorous stirring for 48 h at 40 °C. The pH was then adjusted to 7.0 with NaOH 0.1 M and samples were thus analyzed in their fully ionized form. When necessary, a solution of salt at the required concentration was added to the previously prepared aqueous polymer solution. The resulting mixtures were stirred for a further 24 h at 40 °C and then allowed to stand for at least 24 h at room temperature before measurements were performed. The concentration (Cp) range of alg-g-PCL solutions lies between 5 and 25 g L^{-1} and almost all measurements have been realized at 20 g L^{-1}. This concentration range, corresponds to the semi-dilute regime (see Section 2.2**), over the critical concentration Ccr for all considered samples (Colinet et al., 2009). The solution was left on the rheometer plate for 10 min before starting the experiment in order to allow the recovery of its rheological properties after placing it on the geometry.

3. Results and discussion

3.1. Behaviour in pure water

3.1.1. Effect of the PCL grafting amount

Flow curves of both alg-g-PCL series (i.e. 1250-*x* and 530-*x*) at constant polymer concentration (Cp = 20 g.L^{-1}) in pure water have been plotted on Fig. 2a. In these experiments the shear rate was increased up to 1000 s^{-1} for 20 min. A Newtonian plateau at low shear rates (from 0.01 to 10 s^{-1}) and a slight shear-thinning behaviour for higher shear rates are evidenced for the alginate precursor. At low shear rates, alginate derivatives evidence higher viscosities than the precursor. It is more pronounced when both grafting rate and/or hydrophobe chains length increase. This is the consequence of intermolecular hydrophobic associations. Modified polymers show a markedly typical shear-thinning behaviour upon increasing the shear rate, due to the progressive rupture of the weakly hydrophobic bounds (Candau & Selb, 1999; Volpert, Selb, & Candau, 1998). The absence of a Newtonian plateau occurring for modified samples may indicate the existence of 'yield stresses'. On Fig. 2b, we have reported both increasing (20 min) and decreasing (20 min) stress sweeps for the most grafted alginates (i.e. 1250-13.5 and 530-15) together with the precursor. Unlike alginate it was found that both amphiphilic derivatives require time to return to their initial state when the shear rate is decreased. This result clearly evidences a typical thixotropic behaviour which is more pronounced for the longer PCL chain (i.e. 1250). It appears that the reorganisation of hydrophobic associations is not an instantaneous process. This has been already shown for many associative

Table 1
Physicochemical characteristics of alginate and alginate-g-PCL in dilute regime (from Colinet et al., 2009).

	$\overline{\mathrm{Mn}}$ (g mol^{-1})	$\overline{\mathrm{Mw}}$ (g mol^{-1})	Rh (nm)	$[\eta]$ (NaCl 0.1 M) (mL g^{-1})	K_{H} (NaCl 0.1 M)	Ccr (water) (g L^{-1})	Ccr (NaCl 0.1 M (g L^{-1})
Alginate	194,000	342,000	62	1050	0.36	5.1	6.3
530-4	207,000	390,000	61	834	0.68	3.4	3.6
530-8	210,000	425,000	63	686	0.84	2.6	4.0
530-15	290,000	618,000	85	464	1.01	2.2	4.4
1250-3.5	248,000	524,000	92	740	0.75	3.2	4.2
1250-7.5	342,000	733,000	115	563	0.88	2.5	3.5
1250-13.5	387,000	993,000	128	370	1.15	1.9	2.7

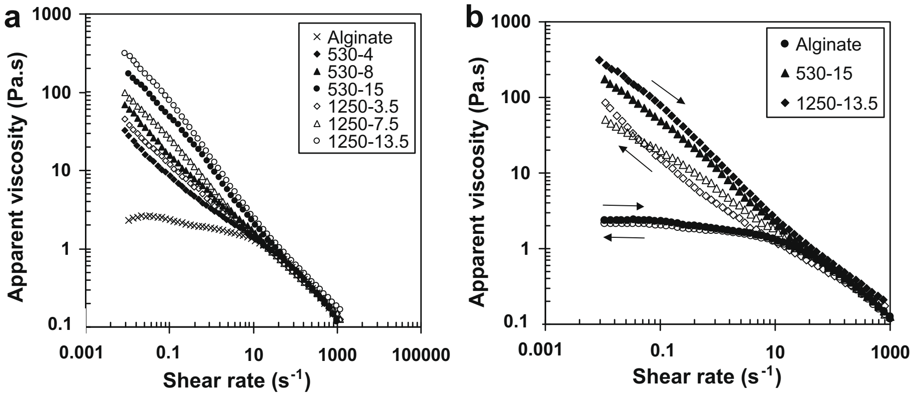


Fig. 2. Viscosity dependence on shear rate for alginate and alginates-g-PCL (Cp = 20 g L^{-1}) (a) and for alginate and two samples of alginates-g-PCL (530-15 and 1250-13.5) during return scaling (filled symbols: increasing of shear rate, open symbols: decreasing of shear rate) (b) (Cp = 20 g L^{-1}) in water, 25 °C.

polymers and notably hydrophobically modified polysaccharides (Charpentier-Valenza, Merle, Mocanu, Picton, & Muller, 2005).

Both storage (G') and loss (G'') moduli of 20 g L^{-1} solutions of alginate and alginates-g-PCL (1250-*x* and 530-*x*, respectively Fig. 3a and b) have been reported as a function of frequency. Mechanical properties of modified alginates strongly differ from those of the precursor with larger values of both moduli. The behaviour of the amphiphilic polymers appears mainly elastic ($G' > G''$) whereas the precursor is mainly viscous ($G'' > G'$). As expected, due to hydrophobic interactions, moduli also increase when both grafting rate and PCL chain length increase. The cross-over point between G' (ω) and G'' (ω) corresponds to ω_{cross}. It is visible for the precursor and for the lower amount of grafted PCL i.e. 1250-3.5 and 530-4. Such behaviour is typical of viscoelastic fluids. The dynamics of the system can be characterized by the corresponding relaxation time ($\tau_c = 1/\omega_{\text{cross}}$). We found relaxation times of approximately 0.05 s for alginate, 0.2 s for 530-4 and 5 s for 1250-3.5. It indicates that the dynamics of disentanglement is slowed by hydrophobic associations and such phenomenon is more pronounced when the PCL chain is longer. Increase of either amount or length of hydrophobic pendant groups shifts the ω_{cross} toward lower frequencies. Consequently τ_c cannot be observed for the more grafted samples. Such systems undergo a sticky reptation dynamic i.e., a reptation hindered by an association/dissociation process (Aubry & Moan, 1994; Charpentier-Valenza et al., 2005; Leibler et al., 1991). Therefore, most derivatives (530-8; 530-15; 1250-7.5 and 1250-13.5) show a mainly elastic behaviour in the studied frequency range. For the 1250-13.5, both G' and G'' are practically frequency-independent (at least in the frequency range covered) and G'/G'' is of the order of 0.2, which is characteristic of a strongly structured liquid sometimes also called ‘pseudo-gel’ (Glinel, Huguet, & Muller, 1999). Consequently, intermolecular hydrophobic interactions seem to act as strong physical cross-links leading to an elastic structural network.

Storage and loss moduli (taken at 10 Hz) have been plotted as a function of grafting rate for 530-*x* and 1250-*x* samples (Fig. 4). Both moduli increase when increasing grafting rate and/or length of the PCL chain. Obviously this is much marked for longer PCL chains. Therefore, and not surprisingly, intermolecular hydrophobic interactions are stronger when hydrophobicity of the polymer increases It seems that a G' plateau could be reach indicating that a critical degree of grafting may occur. Unfortunately we not prepare samples having a higher amount of PCL.

3.1.2. Effect of the polymer concentration

In order to complete the rheological characterization of these systems, the effect of the concentration has been followed for the most structured sample i.e. 1250-13.5. Flow curves experiments have been conducted between 5 and 25 g L^{-1} (Fig. 5). Whatever the concentration, this sample shows a strong shear-thinning behaviour with no evidence for a Newtonian plateau even at relatively low shear rate of 0.1 s^{-1} (Probably an evidence of ‘yield stress’). Above 5 g L^{-1}, a thixotropic behaviour appears indicating that the global relaxation of the structure occurs for longer time than that of the experiment (20 min up/20 min down). Not surprisingly the shear viscosity increases with the concentration due to

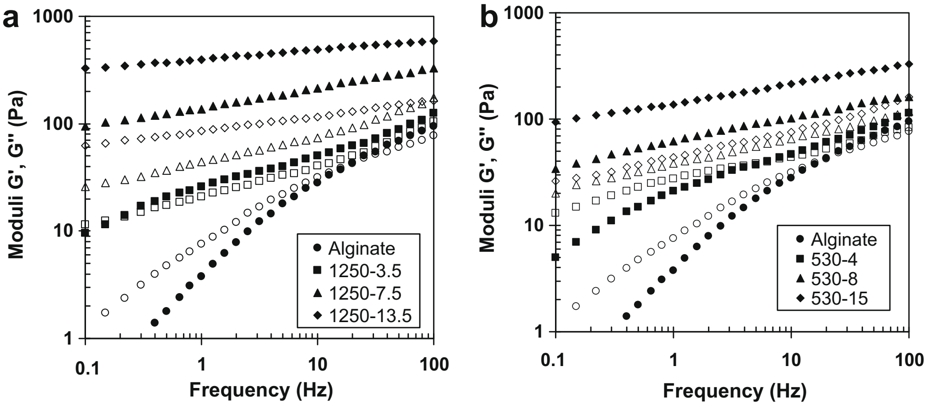


Fig. 3. Storage (G’: filled symbols) and loss (G'': open symbols) moduli versus frequency of alginate and alginates-g-PCL with M_{PCL} = 1250 g mol^{-1} (a) and M_{PCL} = 530 g mol^{-1} (b) at Cp = 20 g L^{-1} in water, 25 °C.

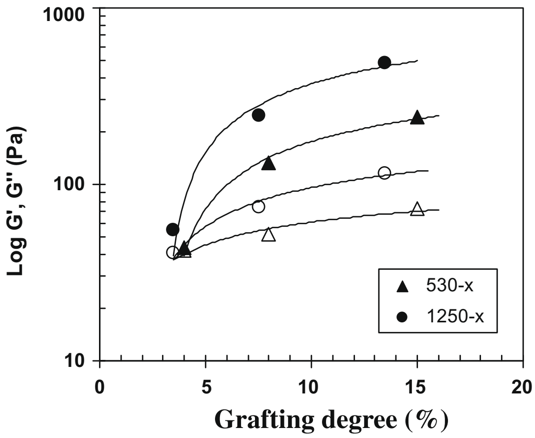


Fig. 4. Storage (G': filled symbols) and loss (G'': open symbols) moduli at 10 Hz versus grafting degree of 530-*x* and 1250-*x* derivatives at Cp = 20 g L^{-1} in water, 25 °C.

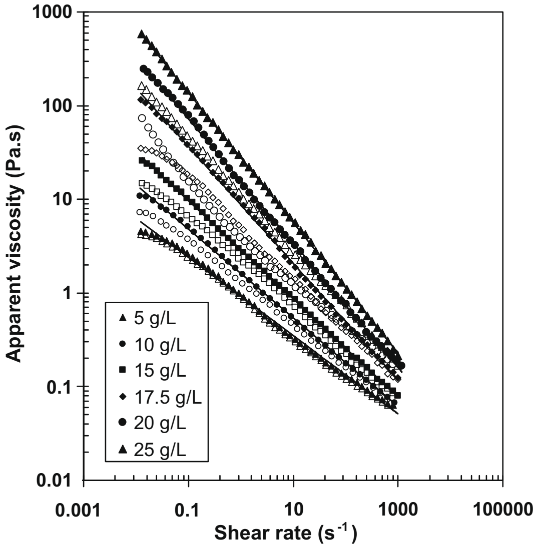


Fig. 5. Viscosity dependence on shear rate for 1250-13.5 as a function of concentration in water, 25 °C.

stronger hydrophobic associations. The viscosity profiles reveal that the shear-thinning behaviour yields a power-law region with different slopes according the concentration:

$$\eta = a(\dot{\gamma})^{-n} \qquad (1)$$

where η is the shear viscosity,$\dot{\gamma}$ is the shear rate and n is the power-law index fitted to the increasing part of the flow curves (the longer n, the more non-Newtonian the behaviour it is). In Table 2, we reported, for various concentration, viscosities at 0.01 and 500 s^{-1}, their ratio, the power-law index and the thixotropic gap $(\eta_{0.01s^{-1}(\rightarrow\dot{\gamma}_{max})} - \eta_{0.01s^{-1}(\rightarrow\dot{\gamma}_{min})}$ with 20 min for both increasing and decreasing sweeps. For all the above mentioned parameters, a strong increase of their values is observed above a critical concentration. It seems that a transition from viscoelastic to strongly structured liquid behaviour occurs in the vicinity of 16 g L^{-1}. We can propose that such systems evidence a rheological transition due to a critical amount of associated domains hindering the chain reptation in the considered time.

3.1.3. Effect of the temperature

The influence of temperature for different concentrations of the most associative sample (i.e. 1250-13.5) in aqueous solutions is reported on Fig. 6. Usually for hydrophobically modified water-soluble systems, increasing temperature induces a notable diminishing of rheological properties (Picton & Muller, 1996; Selb et al., 1997; Volpert et al., 1998). These results are generally explained by the predominance of the hydrophilic character of such systems. The behaviour of sample 1250-13.5 at a concentration lower than 'transition' concentration (15 g L^{-1}) agrees with this conclusion. In contrast and as a confirmation of the discussed transition, it clearly appears that associative behaviour at higher concentrations is not affected by temperature (both moduli are almost constant). It seems to evidence that association become stronger than Brownian motion induced by thermal agitation. This point is particularly interesting because associative polymers with non-temperature dependent rheological properties are not usual.

3.2. Effect of ionic strength on the rheological behaviour

In our previous work (Colinet et al., 2009), it has been shown that the semi-dilute behaviour of 1250-*x* greatly differs from that of 530-*x* in the presence of ionic strength. It was concluded that alginates-g-530 may establish interesting hydrophobic clusters even in the semi-dilute regime where polymer entanglement begin.

Mechanical spectra (i.e. G' and G'' vs. frequency) are shown for 1250-*x* and 530-*x* at Cp = 20 g L^{-1} (respectively, Fig. 7a and b) as a function of PCL amount (*x*) in presence of a ionic strength (NaCl 0.1 M). One can notice a clear elastic behaviour of 1250-*x* in the presence of salt, even for the sample with the lowest grafting rate which was only viscoelastic in pure water (Fig. 3). Consequently, hydrophobic interchain connections are promoted by screening of electrostatic repulsions. These derivatives seem promising as excellent thickening or gelifying agents in salt media. In contrast, alginates-g-530 (Fig. 7b) show a change in rheological behaviour from viscoelastic for the lower grafting rate (i.e. 4%) to clearly viscous for the higher grafting rate (i.e. 15%). This very original phenomenon appears more clearly by plotting the values of G' at 10 Hz as a function of grafting rate for both 530-*x* and 1250-*x* derivatives (respectively, Fig. 8a and b), in pure water and in salt media. This representation shows the opposite effect of ionic strength to the rheological behaviour of the 1250-*x* and the 530-*x* derivatives.

These results obtained in semi-dilute regime (i.e. entanglement state) agree well with our previous observation (Colinet et al.,

Table 2
Values of the power-law index (n), difference between viscosity at 0.01 and 500 s^{-1} and its ratio, and thixotropic gap $(\eta_{0.01s^{-1}(\rightarrow\dot{\gamma}_{max})} - \eta_{0.01s^{-1}(\rightarrow\dot{\gamma}_{min})}$ of solutions of 1250-13.5 at different concentrations in water, 25 °C.

	5 g L^{-1}	10 g L^{-1}	15 g L^{-1}	17.5 g L^{-1}	20 g L^{-1}	25 g L^{-1}
η	0.40	0.45	0.48	0.64	0.68	0.73
$\eta_{0.01s^{-1}}$	3.4	6.7	13.2	67.4	120	225
$\eta_{500s^{-1}}$	0.07	0.09	0.11	0.18	0.27	0.37
$\eta_{0.01s^{-1}}/\eta_{500s^{-1}}$	51	77	120	375	450	608
$(\eta_{0.01s^{-1}(\rightarrow\dot{\gamma}_{max})} - \eta_{0.01s^{-1}(\rightarrow\dot{\gamma}_{min})}$	0.3	3.6	10.1	80	174	416

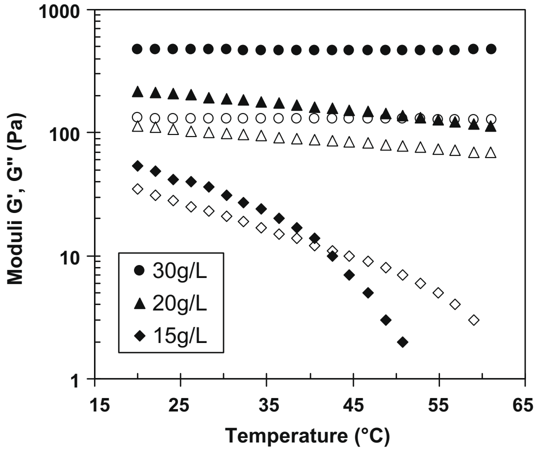


Fig. 6. Storage (G': filled symbols) and loss (G'': open symbols) moduli versus temperature of 1250-13.5 sample as a function of concentration in water at 1 Hz, 25 °C.

2009). Consequently, it clearly appears that for the 530-*x* samples the screening of charges the establishment of hydrophobic clusters together with an entangled structure, even at high concentration. We try to represent schematic pictures of these systems on Scheme 1. Such system (i.e. alginates-g-530) could be of great interest for elaborating controlled release systems targeting hydrophobic compounds.

4. Conclusion

Rheological behaviour of alginate derivatives have been studied in pure water as a function of PCL grafting degree and length, polymer concentration and temperature. In pure water both series of hydrophobically modified alginates behave as classical associative polymers. Flow properties evidence strong shear-thinning behaviour with noticeable thixotropy due to the establishment of time-dependent intermolecular hydrophobic associations. Such behaviour is logically reinforced when increasing either the amount or length of PCL chain (i.e. hydrophobicity of polymer). Increasing of polymer concentration in the case of the most associative system (1250-13.5) leads to an abrupt rheological transition when the dynamic of disentanglement is strongly slowed down. Above this transition an interesting non-dependant temperature rheological profile has been evidenced.

In the presence of salt (i.e. NaCl 0.1 M), hydrophobic associations are reinforced due to the screening of negative charges. Intermolecular associations are improved for the 1250-*x* series leading to stronger physical networks, than in pure water. In contrast, for 530-*x* samples, adding salt decreases the rheological properties from viscoelastic to viscous behaviour leading to a probable increase in hydrophobic clusters. In this range of concentration where entanglements are maintained, it is still possible to obtain physically or covalently bonded hydrogels. These derivatives thus appear as adequate precursors for the synthesis of biodegradable and biocompatible amphiphilic hydrogels, suitable for entrapment and controlled release of hydrophobic or amphiphilic compounds. This will be the subject of a future study.

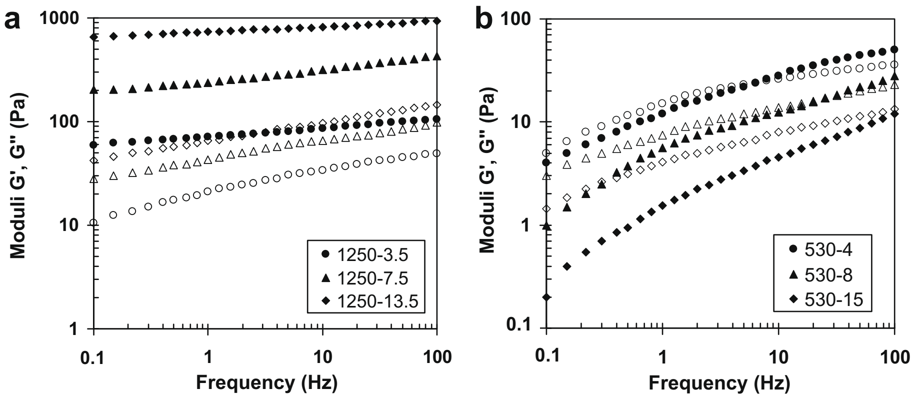


Fig. 7. Storage (G': filled symbols) and loss (G'': open symbols) moduli versus frequency of alginate and 1250-*x* (a) and 530-*x* (b) derivatives at Cp = 20 g L^{-1} in NaCl 0.1 M, 25°C.

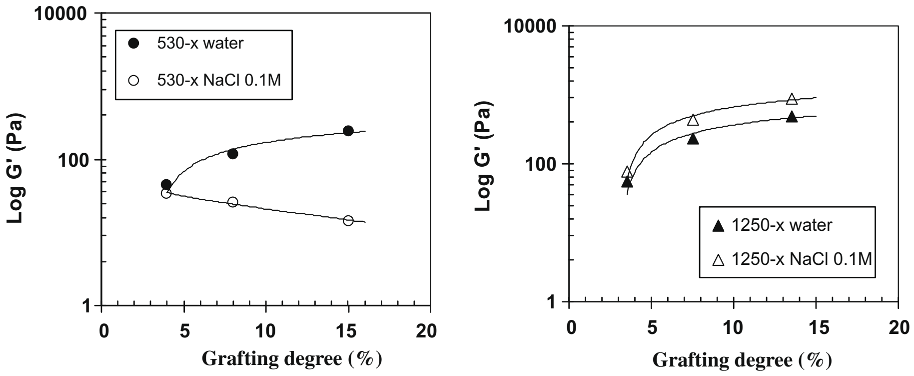
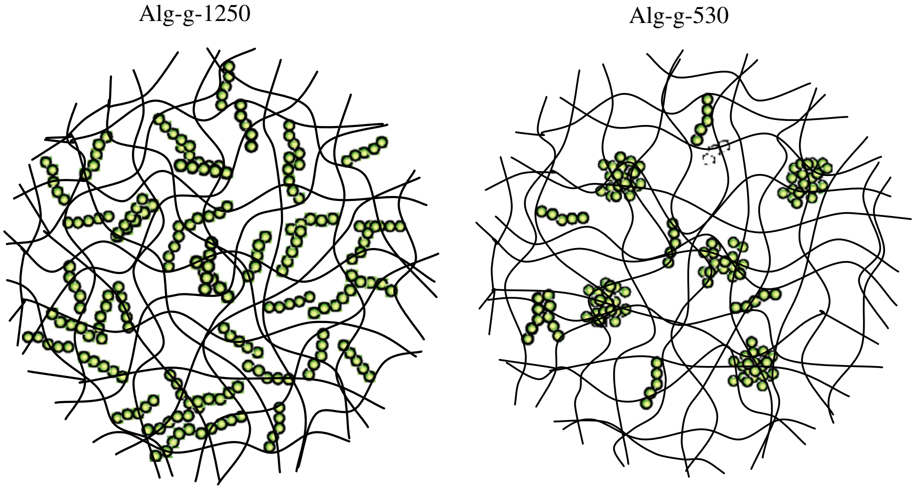


Fig. 8. Storage modulus (G') at 10 Hz versus grafting degree of alginates-g-PCL with M_{PCL}=530 g.mol^{-1} (a) and M_{PCL} = 1250 g mol^{-1} (b) at Cp = 20 g L^{-1} in water and NaCl 0.1 M, 25 °C.



Scheme 1. Schematic of proposed structure of alginates-g-PCL in salt media.

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