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One-pot synthesis and gelation by borax of glycopolymers in water†

Etienne Audebeau, Evdokia K. Oikonomou, Sophie Norvez* and Ilias Iliopoulos‡

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A glycosylated polyamine is synthesized using a straightforward route in aqueous solution. An optimum of grafting is obtained when equimolar amounts of gluconolactone and NaOH are added to an aqueous solution of poly(allylamine hydrochloride), PAH. Under these conditions, up to 60% of gluconolactone is grafted onto the PAH chain, the remaining being transformed into gluconate. The very fast grafting reaction, completed in less than 5 minutes at room temperature, may be applicable to a large range of water-soluble polymers bearing amino groups. Upon addition of borax before any purification process, the reaction mixture can be transformed *in situ* into a hydrogel. The gelation is attributed to the formation of borate diesters acting as cross-linkers of a number of PAH chains bearing glycosylated grafts. The viscoelastic properties of the gels can be triggered by the amounts of gluconolactone and borax incorporated in the mixture as well as by the final pH. Owing to the remaining ammonium groups along the chains which stabilize the borate complex, gels can be obtained at physiological pH, a performance superior to those obtained with comparable poly(vinyl alcohol)- or guar/borax systems.

Introduction

Synthetic polymers containing sugar moieties, also known as glycopolymers, have attracted the attention of the chemistry community over a number of years.[1–4] Glycopolymers not only are used as oligosaccharide surfactant polymers in industrial applications,[5] but also they are recognized as biomimetic analogues of natural glyco-conjugates which play an essential role in numerous biological processes.[6,7] To achieve biofunctionality, proper control of the molecular weight distribution and the macromolecular architecture has to be achieved. Therefore, considerable endeavours have been devoted to the synthesis of glycopolymers with well-defined linear, dendritic, star or bloc architectures.[1,4,8]

Among the various types of glycopolymers, those based on vinyl backbone bearing pendant sugar moieties have received particular attention. They are synthesized either by (co)polymerization of sugar-containing monomers (glyco-monomers) or by chemical modification of preformed polymers. Polymerization of glyco-monomers offers superior control of the polymer architecture especially using modern controlled polymerization techniques, like nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), ring opening metathesis polymerization (ROMP), *etc.*[1–3,7–14] However, the synthesis of glyco-monomers may be challenging and time consuming, requiring multi-step reactions and complex purification procedures. From a practical point of view, such complex synthesis procedures are of interest mostly for specific, high added-value applications as for instance pharmaceutical or biomedical applications.

On the other hand, for less demanding technological applications like paints, wastewater treatment or fluids for petroleum industry for example, modification of pre-existing polymers is an attractive option especially when the reactants, polymer backbone and sugar counterpart are commercially available. Even though the polymers obtained by this technique have a less controlled structure, their final properties are in general fully satisfactory for the aforementioned applications. Compared to the glyco-monomer synthesis route, polymer modification processes are most often simpler, faster, less expensive and easier to scale up. Moreover, post-polymerization glycosylation has revived in the last decades, thanks to the use of highly efficient and selective click reactions, prominently alkyne–azide coupling, thiol–ene addition, as well as coupling of active esters with amines.[3,4,13] Among them, the coupling of amines with lactones is of most interest since it allows the facile modification of polymers bearing amino functionality. Saccharides can easily be transformed into lactones by oxidation of their reducing end-group and dehydration, and subsequent reaction with amines yields amides.[15] Alternatively, pre-existing lactones can be directly reacted with the amino-polymer.[5,8,9,16,17] This coupling reaction has been merely used for the synthesis of

Matière Molle et Chimie, ESPCI ParisTech-CNRS, UMR-7167, 75005, Paris, France. E-mail: sophie.norvez@espci.fr; Fax: +33 1 4079 5117; Tel: +33 1 4079 5113

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‡ Present address: ARKEMA, Research and Development Division, Colombes, France.

glyco-monomers or surfactants, yet very rarely for polymer modification. Moreover, to the best of our knowledge, this polymer modification reaction has never been done in water, and the procedures described in organic solvents require several hours or days.[5,18] Herein, a very simple system based on commercial poly(allylamine hydrochloride) (PAH) and δ-gluconolactone (δ-Glu, a reactant readily obtained from oxidation of δ-glucose) is investigated. Our aim was first to study the grafting reaction of δ-Glu onto PAH in aqueous solvent and also to explore the ability of the resulting Glu-PAH glycopolymers to behave as rheology additives for aqueous formulations.

Indeed, there is still a high demand for thickeners in food, cosmetics or adhesive industry,[19] or for high viscosity fluids able to transport materials in hydraulic fracturing processes,[20,21] and cross-linked water-soluble polymers have long appeared as an efficient means for such operations. Hydrogels are a fascinating class of materials that display a rich behaviour which can be tailored for numerous applications.[22,23] In particular, hydrogels made of hydroxylated polymers crosslinked by borax have been extensively studied in the past, in particular in cases of poly(vinyl alcohol) (PVA)[24–27] or polysaccharides like guar gums.[20,28–35]

In this work the gluconamide-grafted polymer is obtained by simply mixing PAH and δ-Glu in water in the presence of NaOH. The reaction is very fast at room temperature and the grafting reaches 60% efficiency. Meanwhile the remaining gluconolactone is hydrolysed into anionic gluconate. Upon addition of borax in the liquid reaction mixture, reversible gels are formed *in situ*. The viscoelastic properties of these hydrogels depend on the degree of grafting, the borax concentration and the pH. This behaviour is discussed in terms of borate diester formation between gluconamide grafts belonging to different Glu-PAH chains.

Experimental section

Materials

Poly(allylamine hydrochloride) (PAH, M_w = 120–200 kg mol^{-1}, Polysciences Inc.), *D*-(+)-glucono-1,5-lactone (δ-Glu, 99%, Alfa Aesar), sodium tetraborate decahydrate (borax, $Na_2B_4O_7 \cdot 10H_2O$, 99%, Aldrich), deuterium oxide (D_2O, 99.97% D, Euriso-Top), and sodium deuteroxide (NaOD, 30 w/w% solution in D_2O, Alfa Aesar) were used as received. PAH contains 10% residual water as shown by elemental analysis which was taken into account in all experiments. Deionized water was produced with a Milli-Q Integral 3 (Millipore).

^{1}H Nuclear magnetic resonance analysis

^{1}H NMR spectra were recorded in D_2O in a Bruker Avance 400 spectrometer using the following conditions: spectral width 8 kHz, flip angle of 30°, recycling time 3 s, number of scans 4, and temperature 25 °C. Under these conditions, all the protons were fully relaxed.

PAH used in NMR experiments was purified prior to use by dialysis against water and freeze-drying. A stock solution was prepared by dissolving 0.51 g (5 mmol, accounting for 10% residual water in the solid) of purified PAH in 9.5 g D_2O. Final solutions (≈ 5 w/w% in PAH) were obtained by mixing 1 g of the stock solution with adequate amounts of δ-Glu powder and NaOD solution. After 15 s of vigorous mixing, the solutions were poured in NMR tubes, transferred immediately to the spectrometer and equilibrated for 3 min prior to recording the spectra.

Rheology

Rheology measurements were performed at 20 °C in an Anton Paar Physica MCR 501 rheometer coupled with cone/plate geometry (diameter 50 mm, angle 2.012°) operating in the strain-controlled mode. Frequency sweeps were conducted at 10% deformation. Strain sweeps confirmed that the measurements were in the linear viscoelastic regime.

Preparation of mixtures for rheology and phase diagram

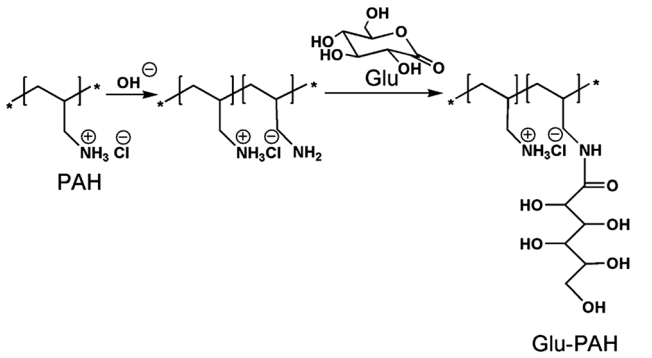
An aqueous stock solution of PAH (10 w/w%) was prepared by stirring overnight. Borax stock solution (5 w/w%) was first heated for 15 min at 70 °C for dissolution and then allowed to cool down to room temperature. The final solutions were obtained by mixing 2 g of PAH stock solution and appropriate equimolecular quantities of δ-Glu in solid form and NaOH in 1 mol L^{-1} solution. After stirring for 15 min, the desired volume of borax solution was added. A detailed description of this procedure is available in the ESI† for the mixture prepared with $x = y = 0.4$, B/Glu = 0.3. At this step, a precipitate formed which dissolved after stirring (2–8 hours depending on the composition). The pH of the homogeneous solution, initially in the range 3–5, was set to the value of 8 upon addition of NaOH solution (1 mol L^{-1}). The final mass of the mixture was adjusted by adding deionized water to reach a PAH concentration of 5 w/w%. The mixtures were equilibrated for 2 hours before running the first rheology measurement. All mixtures have the same PAH concentration and variable amounts of δ-Glu (0 to 0.35 mmol g^{-1}) and boron species B (0 to 0.17 mmol g^{-1}). The term boron species designs both the trigonal (boric) and tetragonal (borate) forms, *i.e.* [B] = 4 × [borax].

Results and discussion

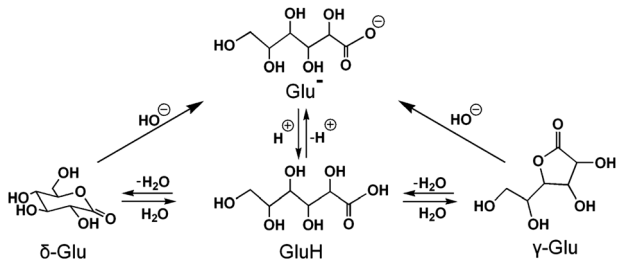
The synthesis of gluconamide-grafted PAH competes with the hydrolysis of gluconolactone

Poly(allylamine hydrochloride), PAH, is transformed into the amine form prior to reaction with gluconolactone, δ-Glu (Scheme 1). The relative fraction of amine units is adjusted by adding NaOH to PAH solution (NaOD for NMR experiments). Gluconolactone reacts readily with primary amines to yield the corresponding gluconamides.[16] The aminolysis of gluconolactone is selective; therefore the protection of hydroxyl groups is not necessary. In solution, δ-Glu is in equilibrium with the γ-Glu isomer and with the open-ring form gluconic acid, GluH, the proportion of each form depending on pH (Scheme 2).[36,37] δ-Glu may also be hydrolysed into gluconate Glu$^-$, especially at basic pH. The grafting reaction will thus be limited by hydrolysis of the gluconolactone, since Glu$^-$ is not reactive towards the amino groups of poly(allylamine).

The grafting reaction was followed *in situ* by ^{1}H NMR. The PAH concentration was kept constant at 5 w/w%, and two



Scheme 1 Synthesis route for the preparation of gluconamide-grafted poly(allylamine hydrochloride) Glu–PAH.



Scheme 2 The different forms of gluconolactone in aqueous solution.

parameters influencing the extent of the modification were varied: the relative amounts of gluconolactone and NaOH. The mixture composition will be given by the relative molar ratios: $x =$ Glu/AH and $y =$ NaOD/AH, where AH represents the monomer unit, Glu and NaOD the quantities of gluconolactone and sodium deuteroxide introduced in the reaction medium. The ^{1}H NMR spectra of PAH (A), Glu (B) and a mixture prepared with $x = y =$ 0.68 (C) are compared in Fig. 1. In the spectral window 2.5–5 ppm, the peaks related to gluconolactone are observed, as well as a broad signal corresponding to the CH_2 protons of the backbone linked to amine or amide groups. Spectra obtained for different y-values may be found in the ESI†. Comparison of the CH_2 broad signal from 2.7 to 3.4 ppm (Fig. 1C, CH_2 referred to 1 and I on the backbone) and the peak at 4.34 ppm (proton a on the graft moiety) allows us to estimate the degree of grafting (the fraction of monomer units transformed into gluconamide). In spectrum 1C, some of the peaks of the gluconate Glu^- may be identified, in particular the protons α' and β'. The grafting reaction is complete within the 5 minutes after mixing the reactants. All the gluconolactone is consumed either by grafting to the polymer (gluconamide) or hydrolysis into gluconate. The ^{1}H NMR spectrum of the mixture does not show any more change in the 8 following hours. It was also checked that no amide formation occurs in the absence of NaOH, attesting that the reactive species is indeed the amine form of PAH.

A systematic study of the relative fraction of the different species was conducted keeping the PAH concentration constant while varying Glu and NaOD concentrations (Fig. 2). For all mixtures the ^{1}H NMR spectra were recorded within the first 15 minutes after mixing. Detailed analysis of the spectra enables us to quantify the various species present in the mixture: gluconamide, gluconate, δ- and γ-gluconolactone (characteristic spectra and their analysis are given in the ESI†). The relative fraction of gluconolactone derivatives observed at the end of the reaction is reported as a function of $y =$ NaOD/AH when the Glu/AH ratio is kept constant at $x = 0.68$ (Fig. 2A) or 1.4 (Fig. 2B), *i.e.* when Glu was introduced either in defect or in excess *vs.* PAH, respectively. The fraction of gluconamide increases continuously up to $y \approx 0.7$ or 1, respectively. Beyond this value, the amide fraction decreases significantly, due to the competition between grafting and hydrolysis. As long as gluconolactone is used in excess compared to NaOD ($x > y$) the grafting reaction is favoured. At higher NaOD concentrations, the hydrolysis reaction competes efficiently with grafting. An optimum of grafting is found at $x = y$, the NaOD/Glu stoichiometry, for all values of $x < 1$. When gluconolactone is used in excess ($x \geq 1$), the optimum of grafting occurs at $y = 1$, when all the monomer units are transformed into the amine form. The excess of NaOD in this case contributes only to the hydrolysis of gluconolactone.

The evolution of the degree of grafting as a function of the ratio $y =$ NaOD/AH is plotted in Fig. 3 for four x values. As a reminder, the degree of grafting is the fraction of AH monomer units transformed into gluconamide. The dashed diagonal line corresponds to the ideal case where the gluconolactone hydrolysis reaction would not occur, allowing the grafting reaction to reach 100% efficiency. For example, for $x = 0.68$, the maximum grafting degree (meaning the maximal modification of the amine form of PAH, which is obtained for $y = x$) would be 68%. Indeed, the maximum of the grafting reaction coincides with the gluconolactone/amine stoichiometry ($x = y$). As a matter of fact, this maximum deviates from the diagonal because of the competition with hydrolysis. The maximum grafting degree for $x = 0.68$ is found at 40%, meaning that the percentage of grafted gluconolactone is only ~60% of the maximum (40/68 = 0.59). The remainder is transformed into gluconate. More generally, the % of grafting, which is found at $x = y$ as long as $x < 1$, or at $y = 1$ for $x > 1$, corresponds to 50–60% of the expected maximum modification.

The conditions imparting maximal grafting will be used hereafter for the rheological experiments.

Addition of borax results in gelation of the glycopolymer

It is well known that polymers carrying diol functionality can form gels in the presence of borax. Borax in aqueous solution releases tetrahedral borate anions $B(OH)_4^-$ able to complex diols to form mono- and di-borate esters as shown schematically in Scheme 3. Chelate binding to the hydroxylated backbone may occur in 5- or 6-membered cycles formed with 1,2- or 1,3-diols, respectively. Efficient cross-linking occurs above the pK_a of borax, *i.e.* at pH > 9.2, when the tetrahedral borate form is stabilized (trigonal boric esters are less stable than their tetrahedral borate counterparts). In the semi-dilute regime, the borate diesters confer viscoelastic properties to the system by acting as transient cross-linkers between the polymer chains. The gel character is defined here by an elastic modulus exhibiting a pronounced plateau extending to times at least of

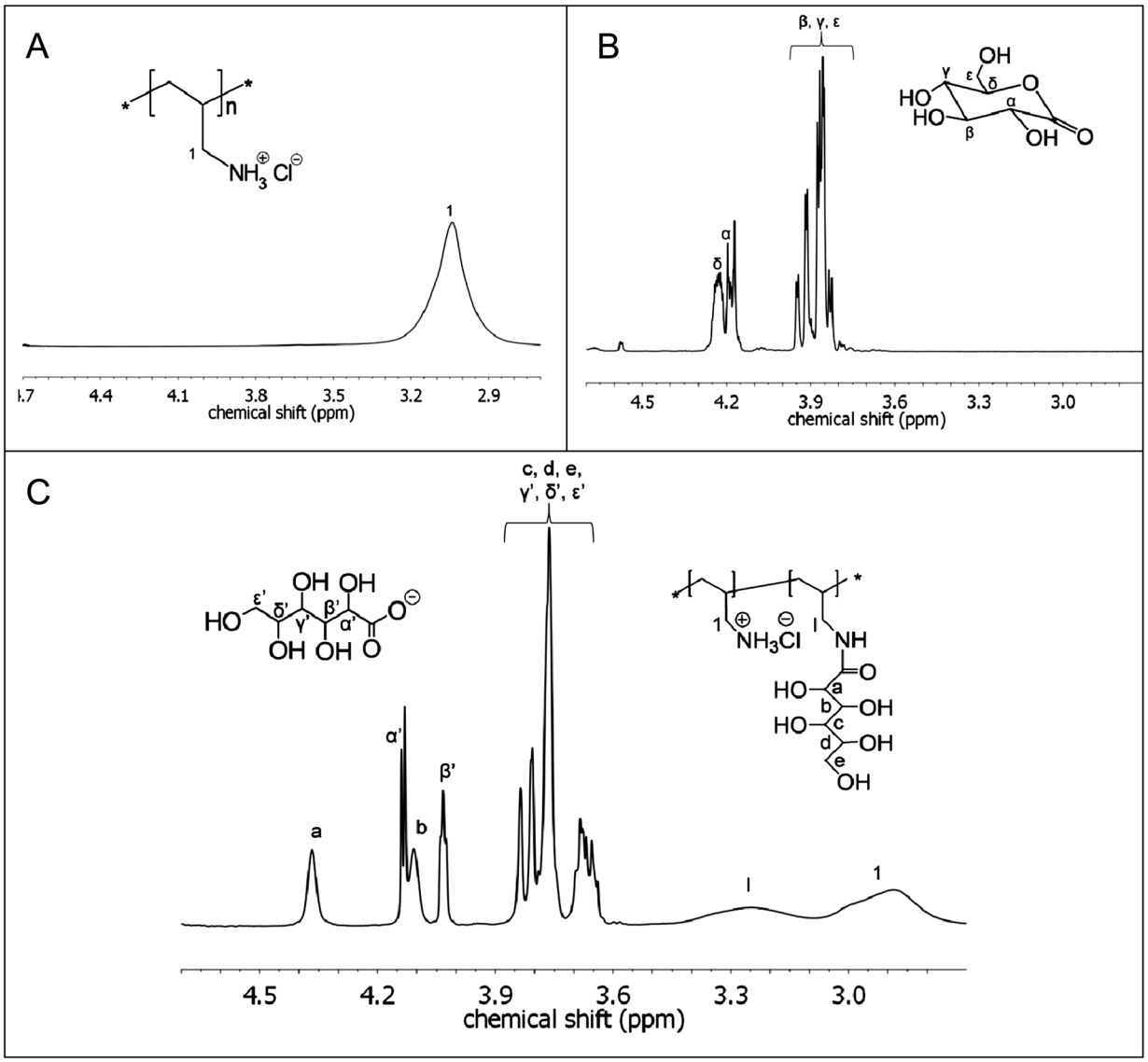


Fig. 1 ^{1}H NMR spectra in D_2O of (A) PAH; (B) gluconolactone; (C) the reaction medium recorded 5 min after mixing the reactants ($x = y = 0.68$). Solvent signal HDO at 4.8 ppm.

the order of seconds and a viscous modulus which is significantly smaller than the elastic modulus in the plateau region.[38]

The grafting of gluconolactone to PAH results in glycopolymers containing a controlled amount of multi-hydroxylated grafts. Each graft has five consecutive hydroxy groups offering various possibilities for borate ester formation. These glycofunctionalized PAHs are therefore good candidates for gelation upon mixing with borax. The gelation study was conducted directly in the reaction mixture without purification of the glycopolymer. Borax was added right after the grafting step (see Experimental part). For rheological experiments, all the mixtures were prepared using equimolar amounts of gluconolactone Glu and NaOH, $x = y$, the conditions for maximum grafting aforementioned. The PAH concentration was kept constant at 5 w/w% and the final pH was set to the desired value by adding NaOH. The rheograms were recorded two hours after the full homogenisation of the mixtures. Typical results are presented in Fig. 4, where either boron or gluconolactone concentration was varied. In Fig. 4A the Glu and base concentrations were set at $x = y = 0.4$ and borax was added at three different concentrations ($C_B = 0.053$ mmol g^{-1}, $C_B = 0.069$ mmol g^{-1}, and $C_B = 0.092$ mmol g^{-1}, corresponding to molar ratios B/Glu = 0.2, 0.3 and 0.4, respectively). The borax concentration refers to all boron species. At lower C_B (B/Glu = 0.1), the mixture is liquid meaning that under these conditions the system behaves like a non-associating polymer solution, or at least that possible associations would be mainly intra-chain. Inversely, when the boron concentration is increased above B/Glu = 0.5 the system phase-separates. In between, the mixture goes from a weak viscous-like fluid at B/Glu = 0.2 to a viscoelastic system at B/Glu = 0.3 and 0.4, with the dynamic elastic modulus G' higher than the loss modulus G'' over a large frequency window. At low frequencies G'' crosses G', the system relaxes and flows, due to an experimental timescale longer than

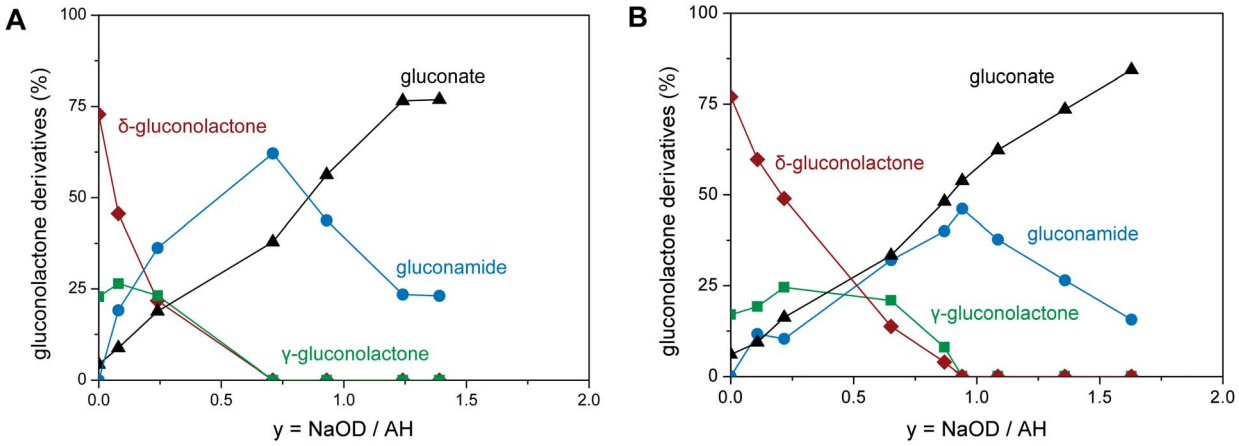


Fig. 2 Relative fraction of gluconolactone derivatives after grafting deduced from ^{1}H NMR analysis of the reaction mixture, as a function of y = NaOD/AH ratio at two different gluconate ratios x = Glu/AH: (A) 0.68; (B) 1.4. PAH concentration 5 w/w%.

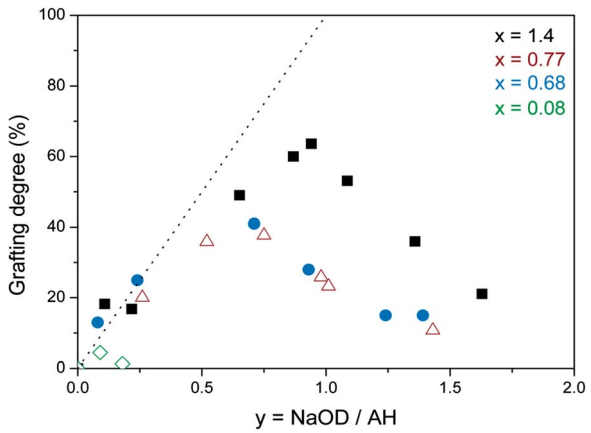
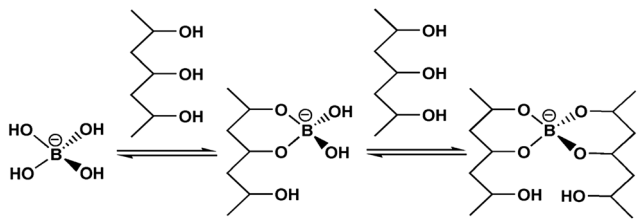


Fig. 3 Degree of grafting as a function of y = NaOD/AH ratio for different gluconamide fractions, x = 0.08 (◇), 0.68 (●), 0.77 (Δ), and 1.4 (■). PAH concentration 5 w/w%.



Scheme 3 Borate ester formation between polyols and borate anions. Borate species are negatively charged. Borate diesters connecting two different polymer chains act as crosslinks contributing to the viscoelastic behaviour of the system.

the lifetime of the kinetically labile bonds, thereby allowing sufficient time for the network to restructure. A characteristic time τ can be estimated using the angular frequency ω_c when $G' = G''$, which demarcates the inverse of the timescale required for crosslinks to dissociate and reform. Here, the crossover frequency ω_c is found in between 3 and 6 mHz corresponding to $\tau = 1/2\pi\omega_c \approx$ 30–60 s. Such relaxation times are relatively long compared with the short ones measured in PVA/borax systems in accordance with the labile character of diol-borate crosslinks (0.1 s).[25] The longer lifetimes observed here may be due to the presence of remaining ammonium groups throughout the PAH chain, which may slow down the kinetics of complex dissociation (*vide infra*).

The evolution of the viscoelastic properties when increasing x, the fraction of Glu and NaOH in the reactive mixture, while keeping the borate concentration constant is presented in Fig. 4B. It is observed that the increase of hydroxyl functionality on the glycopolymer induces strengthening of the gels. The data of Fig. 4 demonstrate that the gluconamide-grafted polymers form gels in the presence of borax and that the elastic character of these materials is enhanced when increasing either the hydroxyl functionality of the polymer or the quantity of cross-linker. It is interesting to note that the increase in hydroxyl functionality (from x = 0.4 to 0.6, Fig. 4B) has only a slight effect on the viscoelastic properties of the system. This is likely due to the fact that most of the borate anions are already bound at x = 0.4 (Glu is in about 3-fold excess to the borate species).

The deep analysis of the viscoelastic behaviour of our systems requires information about the various species of borate anions in the mixture (free, mono-diol ester with the glycopolymer or with the gluconate, and di-diol esters with glycopolymer, gluconate or both). This would require a detailed ^{11}B and ^{13}C NMR study which is out of the scope of the present work.

Compared to the behaviour of guar- or PVA/borax systems which become viscoelastic above pH 9, here gels are obtained at pH as low as 6. The ability of our glycopolymers to gelate at low pH is attributed to the presence of remaining free ammonium groups throughout the PAH; this cationic local environment of the chain may stabilize the tetrahedral borate ester by electrostatic interaction (Scheme 4). The influence of amino groups on the complexation of poly-hydroxylated polymers with phenylboronic acid PBA has been already mentioned in the literature.[39,40] Having cationic amines in the vicinity of PBA has been proposed to facilitate a tetravalent boron state. Indeed, simply

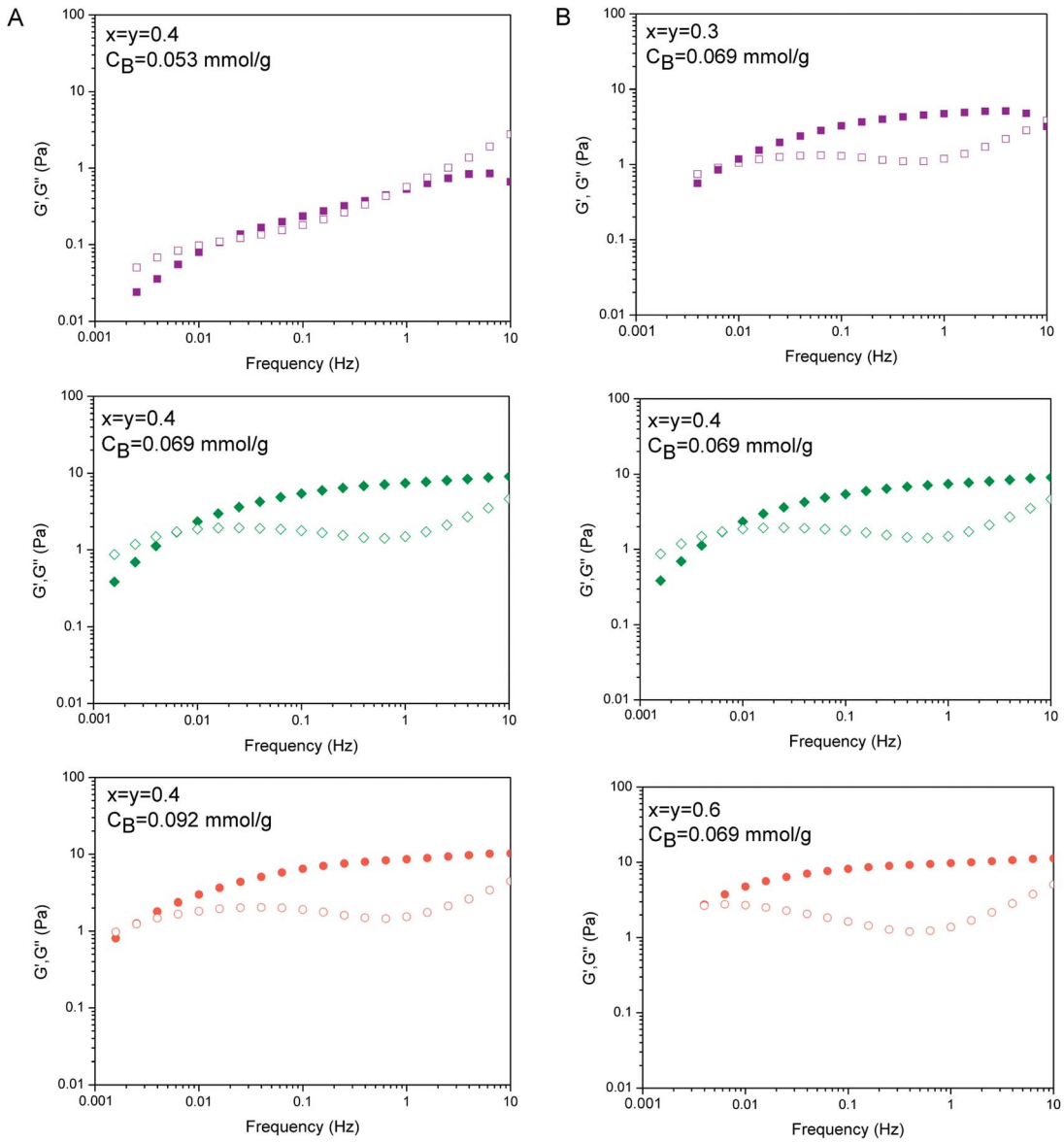
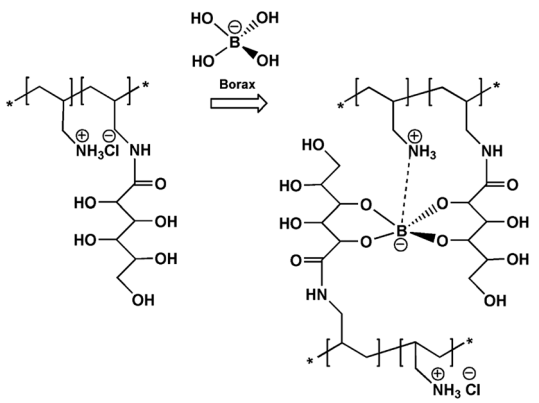


Fig. 4 Viscoelastic behaviour of mixtures prepared (A) by varying the boron concentration C_B at a constant Glu fraction, set at $x = y = 0.4$; (B) by varying fractions of gluconolactone (and NaOH, always with $x = y$) while keeping constant the amount of borax C_B. PAH concentration 5 w/w%, pH was set at 8. G', G'' = full, open symbols, respectively.



Scheme 4 The borate ester complex is stabilized by the remaining ammonium groups along the polymer chain.

placing a quaternized polyamine into a solution containing PBA moieties facilitates sp^3 hybridization of the boron.[41]

A phase diagram implemented under the same conditions as the rheology measurements is presented in Fig. 5 for various (x, C_B) systems. The five previous mixtures are spotted on the graph. At low gluconolactone concentrations ($x < 0.2$), mixtures are liquid whatever be the concentration of borax. Beyond a certain Glu concentration, around $x \approx 0.2$ corresponding to a degree of grafting of about 10%, the rheological state depends on the borax concentration. At low C_B the mixtures are liquid, then the gel phase appears and finally, at high borax concentration, a phase separation occurs (a concentrated white piece of gel is in equilibrium with excess of solvent).

Di-diol esters involving gluconamide grafts from two different PAH chains act as cross-linking points leading to the

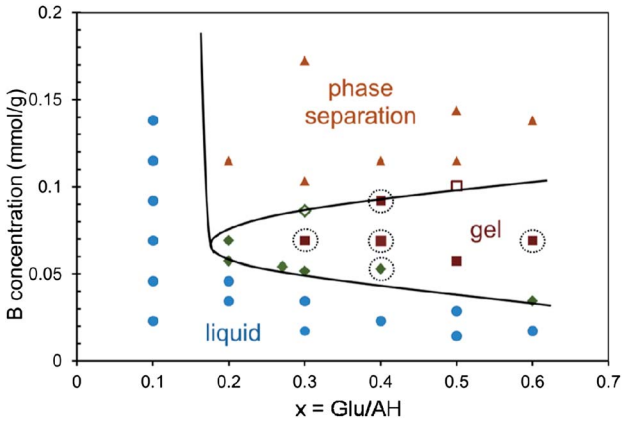


Fig. 5 Phase diagram of PAH/Glu/NaOH mixtures prepared with equimolar amounts of Glu and NaOH ($x = y$). Borax was added after the grafting reaction. The final pH was set at 8. PAH concentration 5 w/w%.

gel formation. The phase separation (collapse of the gel) observed at high boron concentrations is attributed to the increase of the cross-linking density[29] combined with increased attractive electrostatic interactions between the ammonium groups of the PAH backbone and the negatively charged borate esters bound to the polymer. These attractive electrostatic interactions contribute to the deswelling of the otherwise cationic gel.

Besides, it is worthy to note that our one-pot prepared systems contain a significant amount of free gluconate (almost equal to the amount of grafted gluconamide, see Fig. 2) which competes with the gluconamide for association with borax. Still this does not prevent gelation. It is likely that the borate complexation with the gluconamide grafts is more favourable than the one with free gluconate for entropic reasons. The entropy loss when a borate ion associates with a polymer chain

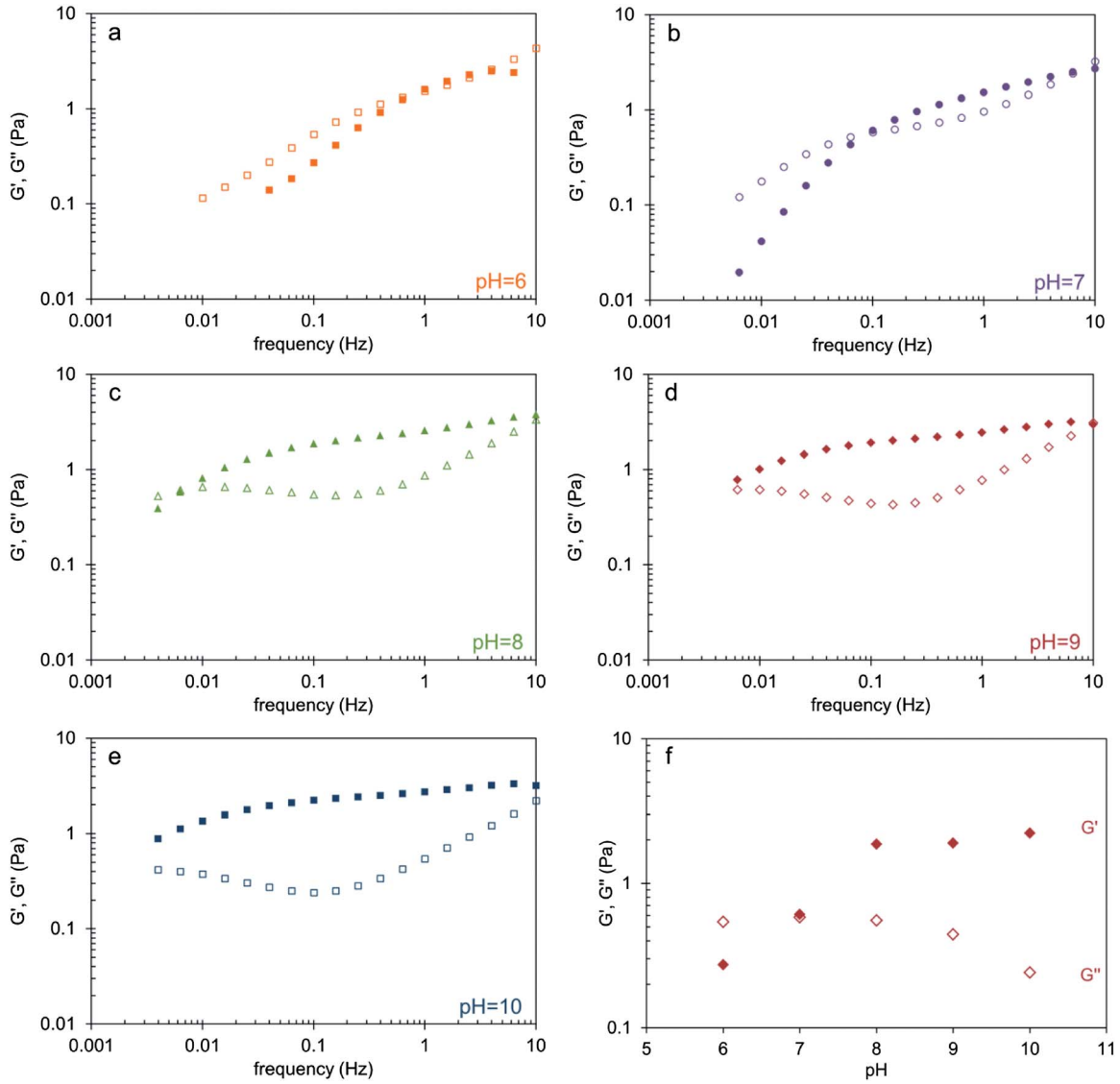


Fig. 6 Influence of pH on the viscoelastic properties of a mixture prepared with $x = y = 0.5$ and B/Glu = 0.2. Measurements were performed 2 h after the complete homogenisation of the mixtures. (a–e) Elastic and loss moduli at different pHs as a function of the frequency; (f) elastic and loss moduli at 0.1 Hz as a function of pH. PAH concentration 5 w/w%.

is lower than that when it associates with free gluconate, while the enthalpic contribution should be comparable in both cases. The gelling process, effective despite the presence of a competitor, demonstrates that our glycopolymers are efficient gel-forming materials.

If we remove the free gluconate, the purified copolymer forms stronger gels in the presence of borax. For example, by purifying a solution such as $x = y = 0.5$ we obtained a purified polymer bearing 27% of grafted Glu. In the presence of borax (B/Glu = 0.2, pH 8) this purified polymer has an elastic modulus that is almost frequency independent and one order of magnitude higher than the corresponding non-purified system. For instance at 1 Hz the elastic modulus increases from 3 Pa (non-purified system) to 40 Pa (purified polymer).[42] However the purification process is time consuming (at least 3 days of dialysis followed by freeze-drying) and has to be repeated for every different degree of grafting. Here we show that the synthesis and the gel formation are possible "one-pot" within minutes. The system has the advantage of being simple, allowing to tune the degree of grafting by varying the amount of gluconolactone and NaOH. Network formation is obtained readily *in situ* despite the presence of competitive molecules, which is much more relevant for industrial applications, for example in the field of water soluble associative thickeners.

Strength and stability of the hydrogel are affected by pH

Boronate esterification is a reversible covalent chemistry which is pH-sensitive. Changes in the pH will in turn affect the stability of the gels. The mechanical spectra of the hydrogels at different pHs are presented in Fig. 6a–e. The behaviour observed at 0.1 Hz as a function of pH is summarized in Fig. 6f. The viscoelastic character already appears at pH 6 and strengthens when increasing the pH. Above pH 8, a plateau zone characterized by a weak frequency dependence of the elastic modulus G' and a marked minimum of the loss modulus G'' are observed, which is associated with strengthening of the gel. This is reflected in the relaxation time τ which increases from 0.1 s to 100 s when the pH is raised from 6 to 10, due to a longer lifetime of the cross-links. At pHs around the pK_a value of the $B(OH)_3/B(OH)_4^-$ couple, exchanges for complex formation and dissociation are slowed down since the concentration of the active $B(OH)_4^-$ increases, which stabilizes the borate diester. Moreover, the negatively charged diester might be stabilized by the NH_3^+ groups remaining throughout the chain. This would explain that our glycopolymers exhibit viscoelastic properties at pHs lower than PVA- or guar/borax comparable systems.[30]

Besides, the hydroxy-amides are sensitive to hydrolysis especially at basic pH. The longevity of our systems, in terms of viscoelastic properties, was checked as a function of time at various pHs (Fig. 7). Up to pH 8, the system does not evolve within the first 4 days. After two weeks however, the drop in the viscoelastic properties is significant. The evolution is faster and prominent under strongly basic conditions; at pH 10, the mixture loses almost completely its viscoelastic character over a single day.

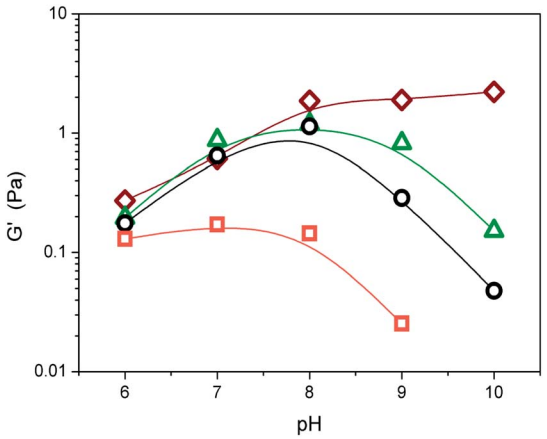


Fig. 7 Evolution over time of the elastic modulus G' of the hydrogels as a function of pH, recorded after: ◇ 2 hours; Δ 1 day; ○ 4 days; □ 2 weeks.

For applications, the pH-sensitivity of both the crosslinks and the backbone should therefore be considered. A pH around 8 appears as a good compromise in terms of viscoelastic properties and stability with age.

Conclusions

A straightforward method for the synthesis of glyco-derivatives of poly(allylamine hydrochloride) (PAH) is presented. Simple and fast, the grafting reaction resulting in gluconamide-grafted PAH is over in less than 5 minutes in aqueous solution at room temperature upon mixing PAH, NaOH and gluconolactone. Under optimum conditions, up to 60% of the gluconolactone available is grafted onto PAH while the remainder is hydrolysed into gluconate.

Viscoelastic gels are obtained *in situ* upon addition of borax without any purification of the glyco-polymer. The gelation is due to the formation of borate diesters favoured by the multivalent character of the glycopolymer, as numerous complexes do act as cross-linkers between the polymer chains. The system presents superior performances than comparable PVA- or guar/borax systems, since here gels are obtained at pH as low as 6, hence at physiological pH, and the strength of the gels can be triggered by the amounts of gluconolactone in addition to the effect of borax and pH.

This work suggests that our simple *in situ* gelling systems may be engineered for applications aimed for example at reducing the permeability of porous media, as it is traditionally applied for the secondary treatment of oil producing reservoirs. Furthermore, the grafting and gelation procedure presented here could be generally applicable to a large range of water-soluble polymers bearing amino functionalities.

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