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Template copolymerisation of *N*-isopropylacrylamide with a cationic monomer: influence of the template on the solution properties of the product

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Abstract

A copolymer containing 91 mol% *N*-isopropylacrylamide (NIPAM) units and 9 mol% *N*,*N*-(dimethylaminopropyl)methacrylamide (MADAP) units, copolymer II, was prepared using polyacrylate chains as a template for the positively charged MADAP units. The properties of this product were compared to the properties of a similar copolymer (copolymer I) prepared in the absence of the template. The molar mass of copolymer II was found much higher than that of copolymer I. Moreover, the cloud point of copolymer II is closer to the cloud point of the homopolymer poly(*N*-isopropylacrylamide) at various pH conditions, indicating that copolymer II contains longer NIPAM-sequences than copolymer I. This explanation is further supported by the fact that copolymer II forms stronger, more compact and more hydrophobic hydrogen-bonding interpolymer complexes with polyacrylic acid at low pH, as it was revealed by viscometry, fluorescence and turbidity studies. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Template copolymerisation; Polyelectrolyte complexes; Hydrogen-bonding complexes

1. Introduction

In template polymerisation [1,2], chain growth occurs mainly along a suitable template polymer, due to the development of special attractive interactions between the monomer or the growing chain and the template. This differentiates effectively the polymerisation process from the usual polymerisation as it affects significantly the kinetics of the reaction and the structure of the daughter chains. Although several secondary attractive forces have been exploited in template polymerisations [1], the most studied cases concern the formation of hydrogen-bonding interpolymer complexes [1–9] or interpolyelectrolyte complexes [1,2,10–18] between the template and the growing chain. Hydrogen-bonding association between weak polyacids and non-ionic polybases or strong electrostatic attractions between oppositely charged polyelectrolytes are, respectively, the driving forces for the formation of the aforementioned interpolymer complexes [19,20].

Excepting some rare cases, template homopolymerisations have been mostly studied. The aim of these studies was to clarify the mechanism of the polymerisation process or to investigate the influence of the template on the microstructure of the daughter homopolymer. As far as we know, efforts to isolate the product are very rare, as the purpose of such studies was either just to investigate the kinetics of the reaction or to use directly the resulting interpolymer complex in special applications.

In the present work, we report the preparation, isolation and physico-chemical study in dilute aqueous solution of a copolymer prepared in the presence of an homopolymer acting as the template for one of the two monomers. This copolymer contains ~90 mol% non-ionic *N*-isopropylacrylamide (NIPAM) units, while the rest 10 mol% is a weak amine-containing basic monomer, the *N*,*N*-(dimethylaminopropyl)methacrylamide (MADAP), Scheme 1. By neutralising MADAP monomers with polyacrylic acid (PAA), these monomers become the counterions of the polyacrylate chains used as the template and they are allocated mainly close to the template, due to counterion condensation [21]. On the contrary, the non-ionic NIPAM units are homogeneously distributed in the reaction solution. This non-uniform distribution of the two monomers in the

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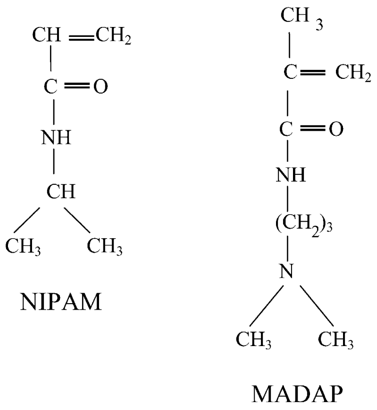

Scheme 1.

reaction solution is expected to be accentuated by the formation of an interpolyelectrolyte complex between the growing chain and the template. As a result, a copolymer of a blocky structure is expected to be formed: as long as the copolymer chain grows along the polyacrylate chain, MADAP- or MADAP-rich sequences should be formed, while NIPAM-rich sequences should be formed, when the chain grows in the solution. On the contrary, the corresponding product prepared in the absence of the template is characterised by a rather random distribution of the two monomers, as their reactivity ratios are quite close [22].

As a result of this difference in the structure of the two copolymers, their ability to form hydrogen-bonding complexes with weak polyacids at low pH is expected to be different. It is well-known that the homopolymer poly(*N*-isopropylacrylamide) (PNIPAM) forms strong, compact hydrogen-bonding interpolymer complexes with PAA [23,24] even at pH as high as 4, that precipitate at lower pH values [25]. At low pH (for instance at pH 2), all MADAP units of the copolymers are positively charged and will disrupt effectively the formation of long hydrogen-bonding sequences between the NIPAM units and the undissociated carboxylic groups of PAA. As a result, hydrogen-bonding association will be weakened. This should be more important for the interaction of PAA with the random copolymer. On the contrary, the blocky copolymer with the significantly longer NIPAM-sequences is expected to maintain a more significant hydrogen-bonding ability with PAA.

Another important reason for choosing NIPAM as the non-ionic monomer component is the well-known lower critical solution temperature (LCST) behaviour of PNIPAM in water, i.e. the fact that PNIPAM is not soluble in water, when temperature increases above 32–34 °C, although it is well-soluble at lower temperatures [26]. This property attracts a continuously increasing interest and linear copolymers or gels of NIPAM already find numerous practical applications, when a temperature-dependent behaviour is desired [27,28]. In our study, cloud point measurements provide an easy and practical tool to detect the structural differences of our copolymers, as they will be reflected in a different way in the LCST behaviour of the products.

2. Experimental

2.1. Materials

The two monomers, NIPAM and MADAP, and the anion-exchange resin DOWEX 1x2-400 were products of Aldrich and used as received. PAA of a nominal weight-average molar mass equal to 5000 was purchased from Polysciences. All other chemicals used were of analytical grade. Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga laboratory unit.

2.2. Synthesis

Both copolymerisations were conducted at 29 °C in pure water. The redox couple $(NH_4)_2S_2O_8/K_2S_2O_5$ was used for the initiation of the reaction, after degassing the solutions for half an hour [29].

The typical copolymerisation reaction was performed after neutralising stoichiometrically MADAP monomers with HCl. The reaction was let to take place for 24 h and then an excess of NaOH was added to turn MADAP units into the non-ionic basic form. The solution was purified by dialysis and the product was recovered by freeze–drying.

For template copolymerisation, MADAP monomers were neutralised stoichiometrically with PAA. During the reaction, phase separation occurred due to the formation of interpolyelectrolyte complex between the product and polyacrylate chains. After 24 h, an excess of NaOH was added to dissolve the product and the solution was mixed with the anion exchange resin under stirring for half an hour. Then, the supernatant was recovered, dialysed to remove low molecular weight species and the product was recovered by freeze-drying.

2.3. Characterisation

The composition of the products was determined by ^{1}H NMR studies and by potentiometric titration of the basic MADAP units.

Their weight-average molar masses, M_w, were evaluated from their intrinsic viscosities, $[\eta]$ (measured in ml/g), in 0.5 M $LiNO_3$ solutions at 20 °C, using the formula [22]:

$$[\eta] = 0.047 M_w^{0.61} \tag{1}$$

2.4. Cloud point measurements

The change of the optical density of the aqueous solutions of the polymers as a function of temperature (or as a function of PAA concentration in the mixtures at 25 °C) was monitored at a fixed wavelength of 490 nm by means

Table 1
Characterisation of the products derived by usual and template copolymerisation

Copolymer	Method of synthesis	MADAP content of the copolymers		Intrinsic viscosity (ml/g)	M_w
		Titration (mol%)	^{1}H NMR (mol%)		
Copolymer I	Usual (homogeneous) copolymerisation	10	9	70	160.000
Copolymer II	Template copolymerisation	9	9	189	800.000

of a Hitachi spectrophotometer model U 2001, equipped with a circulating water bath.

2.5. Viscometry

Reduced viscosity measurements were carried out at 25 °C with an automated AVS 300 viscosity measuring system from Schott–Gerate equipped with a micro Oswald type viscometer. For the intrinsic viscosity measurements, an Ubbelhode type viscometer was used. Temperature was controlled within a precision of ±0.02 °C.

2.6. Fluorescence probing studies

Steady state fluorescence spectra were recorded on a Perkin–Elmer LS50B luminescence spectrometer equipped with a circulating water bath in order to control the temperature of the measuring cell. Pyrene was used as a micropolarity sensitive probe at a concentration 8×10^{-7} M. The excitation wavelength was 334 nm. The change in the intensity ratio (I_1/I_3) of the first (I_1) vibronic band at 373 nm over the third vibronic band (I_3) at 384 nm, of the emission spectrum of pyrene was used to detect hydrophobic microdomains.

3. Results and discussion

3.1. Synthesis and characterisation

The characterisation results of the two copolymers are summarised in Table 1. The random copolymer is referred as copolymer I, while the product synthesised by template copolymerisation is referred as copolymer II. ^{1}H NMR, as well as potentiometric titration confirm that the two copolymers contain ~9 mol% MADAP units, i.e. very close to the feed composition (10 mol%). This was expected for the homogeneous copolymerisation for which it has been shown that the reaction proceeds to a high conversion [22]. Nevertheless, it was not evident for the template copolymerisation, which proceeds under heterogeneous conditions, as phase separation was observed during the reaction due to polyelectrolyte complex formation. Moreover, the observation (see also Fig. 2) that the aqueous solutions of both copolymers at low pH (where all MADAP units are charged) do not turn turbid even upon heating to high temperatures strongly suggests that the products do not contain any important fraction of PNIPAM chains or of low-MADAP content chains. Thus, we should accept that the composition heterogeneity of the copolymer chains of both products is not important, but the copolymer chains are rather uniform of a composition similar to the feed composition.

It is noteworthy that the intrinsic viscosities and consequently the molar masses of the two products are significantly different. The intrinsic viscosity of copolymer I is the expected according to the conditions of synthesis, mainly the ratio of the initiator molar concentration over the monomers molar concentration [22]. Its molar mass is estimated from Eq. (1) to be ~160.000. On the contrary, the intrinsic viscosity of copolymer II, derived by template copolymerisation, is much higher and its molar mass is estimated to be ~800.000. We should note that Eq. (1) is strictly valid only for the homopolymer PNIPAM. Nevertheless, we can accept at a first approximation that it is still valid for our copolymers, as they are highly rich in NIPAM units. We have also observed a similar significant difference for the corresponding copolymers of MADAP with *N*,*N*-dimethylacrylamide prepared under similar conditions (results not presented here). These differences are apparently due to the presence of the template and they should probably be attributed to the well-known high increase of the propagation rate constant observed for template homopolymerisations.

3.2. Cloud point studies

In Fig. 1, we present the influence of temperature on the optical density of dilute aqueous solutions of the two copolymers in 0.01 M NaOH. Under these conditions (pH ~ 12), all MADAP units are in the non-ionic basic form and the copolymers are uncharged. To compare, we have also plotted the corresponding curve of the homopolymer PNIPAM, which exhibits the well-known sharp turbidity increase at 34.8 °C. Due to the absence of charge in the copolymers and the rather low-MADAP content, their aqueous solutions turn strongly cloudy upon heating, similarly to the behaviour of the homopolymer PNIPAM. Nevertheless, the onset of the turbidity increase (cloud point) and the slope of the turbidity curve with temperature are different. As expected [30], for copolymer I (random copolymer) the turbidity change is abrupt similarly to the behaviour of PNIPAM, while the cloud point is displaced at 37 °C. On the

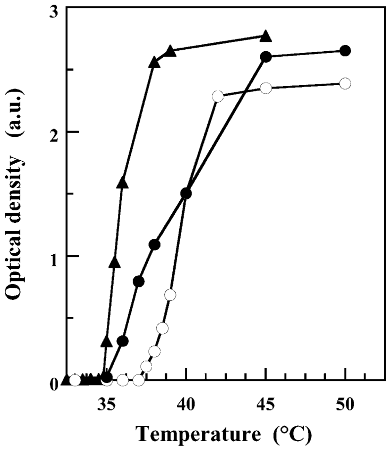

Fig. 1. Variation of the optical density of aqueous PNIPAM (▲), copolymer I (○) and copolymer II (●) solutions with temperature at pH 12. The polymer concentration is 2.5×10^{-3} g/ml.

contrary, the turbidity change of copolymer II (blocky copolymer) is more gradual. Moreover, its cloud point is observed at 35 °C, very close to the cloud point of the homopolymer. The cloud point difference should be attributed to the longer NIPAM-sequences formed in the case of copolymer II, as a result of the presence of the template during the copolymerisation reaction. Furthermore, the gradual turbidity change of copolymer II could arise from the length polydispersity of NIPAM-sequences, reflecting the molar mass polydispersity of the template PAA (which is a product of free-radical polymerisation).

The influence of pH on the phase-separation behaviour of the two copolymers is presented in Fig. 2. The solutions at pH 9 and pH 5 were prepared by addition of an adequate quantity of HCl. By decreasing pH from 12 to 5, MADAP units are gradually neutralised so that the charge content of the copolymer chains increases from 0 at pH 12 to 9 mol% at pH 5 (where all MADAP units are neutralised), while it is intermediate at pH 9 (where MADAP units are partially charged). At pH 5, no phase separation has been detected by turbidimetry, as expected for NIPAM copolymers containing 9 mol% charged units [30]. At pH 9, on the other hand, phase separation takes place, as both solutions turn turbid with increasing temperature. The turbidity increase now is much more gradual compared to the corresponding results at pH 12. Moreover, the cloud points are detected at higher temperatures, namely at 40 °C for copolymer I and 37 °C for copolymer II. Both changes (strength of turbidity, cloud point shifts) are related with the existence of charged units on the copolymer chains. First, it is known that charged comonomers influence much stronger the cloud point of NIPAM copolymers than non-ionic comonomers [31,32]. Second, charges can electrostatically stabilise the phase-separated polymers in their colloidal form. However, the influence of the template is also evident for the results at pH 9, as the cloud point of copolymer II is clearly closer to the cloud point of PNIPAM, as compared to the cloud point of copolymer I. In reality, the problem is much more complicated if we consider also the possibility of charge migration [30], as at pH 9 the MADAP units are only partially neutralised. Nevertheless, the main conclusion derived from the results of Fig. 2 does not change.

3.3. Hydrogen-bonding interactions with PAA

The formation of hydrogen-bonding interpolymer complexes between the two copolymers and PAA was studied in aqueous 0.01 M HCl solutions (pH ~ 2). At this low pH, the dissociation degree of acrylic acid units is very low so that the Coulombic attractions between the two complementary polymers can be ignored. Thus, any complex formation observed should be attributed only to hydrogen-bonding interactions. All the studies presented in the following have been performed at 25 °C using PAA with $M_w = 5000$ and at constant copolymer concentration, 1.5×10^{-3} g/ml.

Fig. 3 presents the reduced viscosity of the copolymers in

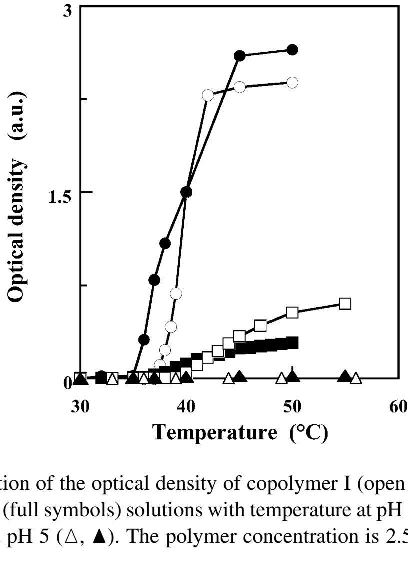

Fig. 2. Variation of the optical density of copolymer I (open symbols) and copolymer II (full symbols) solutions with temperature at pH 12 (○, ●), pH 9 (□, ■) and pH 5 (△, ▲). The polymer concentration is 2.5×10^{-3} g/ml.

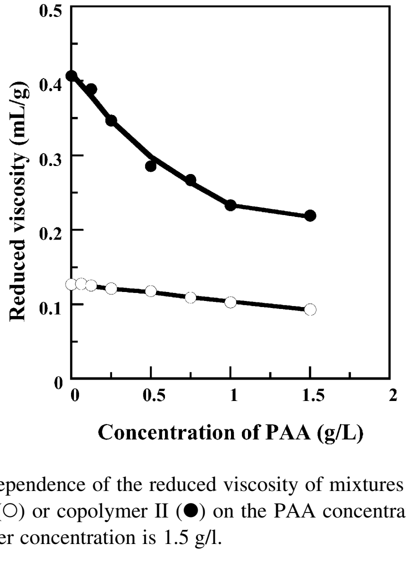

Fig. 3. The dependence of the reduced viscosity of mixtures of PAA with copolymer I (○) or copolymer II (●) on the PAA concentration at 25 °C. The copolymer concentration is 1.5 g/l.

aqueous mixtures with PAA at pH 2 as a function of PAA concentration. The reduced viscosity of the pure copolymer II is much higher than the reduced viscosity of the pure copolymer I, as a result of the great difference of the molar masses of the two products. For the mixtures of both copolymers with PAA, the reduced viscosity decreases as a function of PAA concentration. The decrease is more significant for the mixtures containing copolymer II, whereas it is very smooth for the mixtures containing copolymer I. The fact that a reduced viscosity decrease is observed in both cases provides a good evidence that hydrogen-bonding interactions between PAA and the random (copolymer I) or the blocky copolymer (copolymer II) take place, leading to a more compact interpolymer complex, as it is usually observed with such interpolymer complexes in water. Furthermore, this hydrogen-bonding association of PAA with the random copolymer I seems to be very weak, whereas it is much more important for the mixtures containing the blocky copolymer II.

To our knowledge, in literature there are no studies concerning the influence of the introduction of non-complexable charged units in the polybase chain on the strength of the hydrogen-bonding interpolymer complex formed between non-ionic polybases and polyacids. On the contrary, it is rather well-established that the introduction of 10–15 mol% charged units randomly distributed in the polyacid chain inhibits any hydrogen-bonding interpolymer complex formation between these polyacids and polyethyleneglycol [33–35]. The destructive action of charges in these complexes is double: they disrupt the long polyacid sequences needed for the formation of strong hydrogen-bonding interpolymer complexes and they lead to a chain conformation and chain flexibility not suitable for interpolymer complex formation. From Fig. 3, we can conclude that the interaction of PAA with copolymer I, containing ~10 mol% non-complexable charged MADAP units randomly distributed in the polybase chain, is rather weak. This suggests that the limit for complex formation should be similar regardless of whether the non-complexable charged units are introduced randomly in the polybase chain or in the polyacid chain. This is not surprising, as the destructive action of charges as structural defects is similar in both cases.

On the contrary, hydrogen-bonding interpolymer complexation seems to be much stronger between PAA and the template product II, as the decrease of the reduced viscosity is more pronounced in this case. This should be attributed to the blocky structure of copolymer II, as compared to the random structure of copolymer I. Now, the structure defects, i.e. the charged MADAP units, do not influence effectively the whole polymer chain, but only the MADAP-rich sequences. The NIPAM-rich sequences are less affected and they maintain an important ability to form hydrogen-bonding complexes with PAA.

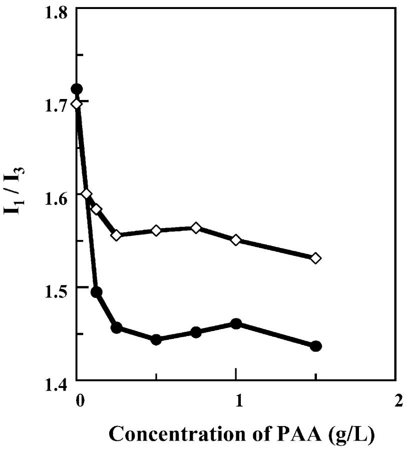

Fig. 4. The dependence of the ratio I_1/I_3 of mixtures of PAA with copolymer I (◇) or copolymer II (●) on the PAA concentration at 25 °C. The copolymer concentration is 1.5 g/l.

Hydrogen-bonding interpolymer association not rarely leads to the formation of complexes with an enhanced hydrophobic character, especially when the polymers involved are rather hydrophobic. In such cases, the ratio I_1/I_3 of the intensities of the first over the third vibronic band of pyrene emission spectrum can be used in order to detect the formation of hydrophobic microdomains in aqueous solution [36]. Here, we have applied this technique for the investigation of the complex formation between our copolymers and PAA at pH 2 (Fig. 4). In the absence of PAA, the ratio I_1/I_3 takes high values, around 1.7, indicative of a hydrophilic microenvironment. Nevertheless, I_1/I_3 decreases substantially by the very first addition of PAA in the solution and very soon it seems to reach a plateau. This plateau is around 1.55 for the complex with copolymer I, whereas for the complex with copolymer II is around 1.45. Note that the lower I_1/I_3 value for the complex of PAA with the homopolymer PNIPAM at pH 4 is around 1.35 [37]. This indicates that copolymer II forms complexes with PAA of an important hydrophobicity, comparable to that of the corresponding complexes formed by the homopolymer. On the contrary, the hydrophobicity of the mixtures of PAA with copolymer I is clearly less significant.

Both interpolymer complexes are characterised by a small turbidity at pH 2, as it is shown in Fig. 5. This turbidity is very low for the mixtures of copolymer I with PAA, whereas it is significant (but not very important) for the complex of copolymer II with PAA. We should remind that the homopolymer PNIPAM forms water-insoluble hydrogen-bonding complexes at pH 2 [25]. Introducing charges on the chains, by increasing pH or by using charged copolymers, has two consequences: first, this weakens interpolymer association as discussed previously in Fig. 3. Second, whenever this association possibly remains strong enough, the introduced charges inhibit the formation of large particles, but they stabilise electrostatically the hydrophobic complex as colloidal microparticles. Our studies suggest that the first reasoning is better valid for the mixtures of PAA with copolymer I: due to the randomly

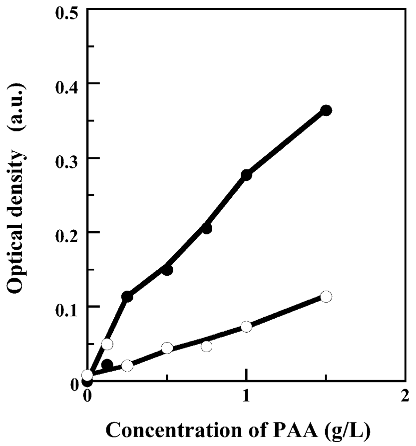

Fig. 5. The variation of the optical density of mixtures of PAA with copolymer I (○) or copolymer II (●) with the PAA concentration at 25 °C. The copolymer concentration is 1.5 g/l.

distributed charges, interpolymer association is very weak and all the three methods used (viscometry, fluorescence probing, turbidity) detect very weak effects. In contrast, the second reasoning seems more suitable for the mixtures of PAA with copolymer II at pH 2: the non-uniform distribution of charged MADAP units allows the longer NIPAM-sequences to form rather strong, relatively compact (viscometry) and substantially hydrophobic (fluorescence study) hydrogen-bonding complexes with PAA. Nevertheless, the size of the compact structures formed is large enough and the turbidity of the system is higher.

4. Conclusions

In this study, we have exploited the charge condensation effect of cationic MADAP units onto a polyacrylate main chain and the interpolyelectrolyte complex formation between polyacrylate chains and MADAP-sequences, in order to prepare by template copolymerisation a copolymer containing charged MADAP and uncharged NIPAM-sequences. The obtained product was isolated by using an anion exchange resin at high pH. The great importance of the presence of the template on the structure of the copolymer is first revealed by the high molar mass of this product, as compared with a copolymer prepared under identical conditions, but in the absence of the template. Moreover, both the method of synthesis and the phase-separation behaviour of the copolymer suggest that this copolymer contains NIPAM-sequences substantially longer than the mean length of the NIPAM-sequences of the copolymer obtained by usual homogeneous copolymerisation. This structural difference of the two products is further supported by the fact that the template product forms stronger, more compact and more hydrophobic hydrogen-bonding interpolymer complexes with PAA at low pH, as it was revealed by viscometry, fluorescence and turbidity studies. Nevertheless, a direct verification of the blockiness of the product by an adequate characterisation method would be undoubtedly helpful.

Template copolymerisation techniques are studied in our research group in the frame of our investigations aiming to the synthesis of copolymers able to form in water strong interpolymer complexes with adequate complementary polymers, while maintaining a good water-solubility. In fact, the synthetic approach adopted in the present study was aiming to a product forming strong water-soluble hydrogen-bonding interpolymer complexes with polyacids, like PAA. This is a difficult and complicated task, as the strength of such complexes is enhanced by lowering pH, while most of these complexes loose their water-solubility at low pH. These first results presented here are indeed very encouraging, as they confirm that the product derived by template copolymerisation can form strong enough hydrogen-bonding interpolymer complexes with PAA at pH 2, while no important macroscopic phase separation takes place. Nevertheless, a slight turbidity is observed, suggesting that the charged complex is electrostatically stabilised as large colloids. Our studies now are focusing towards water-solubility of the complexes in the molecular level, while enhancing even more the strength of interpolymer hydrogen-bonding association. To achieve this, the first structural parameters to be examined are: the nature of the non-ionic component, the length of the template, the composition of the product and its molar mass.

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