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Synthesis and swelling behaviour of hydrophobically modified responsive polymers in dilute aqueous solutions

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Abstract

New series of associating polymers were synthesised in order to investigate opposite behaviours of hydrophobically modified water-soluble polymers and thermoresponsive water-soluble polymers carrying LCST stickers. On the basis of a poly(acrylic acid) backbone, amino-terminated poly(*N*-isopropylacrylamide), poly(ethylene oxide-*co*-propylene oxide) and/or dodecyl chains were grafted following a reaction of condensation activated by carbodiimide. Two homologous series of well-defined single grafted and double grafted copolymers were obtained, with double grafted chains containing both C12 and LCST grafts. The dilute solution properties of these copolymers were carefully studied by capillary viscometry. At low salt concentration and below the LCST of the grafts, the swelling properties of macromolecular chains are controlled either by intramolecular associations between hydrophobes, excluded volume effect exerted by hydrophilic grafts or by a balance between these opposite interactions. The deswelling of macromolecular chains, induced by hydrophobic interactions, is amplified at higher ionic strength and more particularly above the transition temperature of the side chains.

Keywords: Poly(acrylic acid); Associating polymers; Viscometry

1. Introduction

Aqueous formulations exhibiting high viscosities at rather low concentrations of dissolved materials find uses in a wide variety of applications: pharmaceuticals; cosmetics; paints; enhanced oil recovery, etc. [1,2]. Such formulations often contain among others, hydrophobically modified water-soluble polymers (HMP). These polymers are based on a hydrophilic backbone, ionic or non-ionic, to which small amounts of hydrophobic groups (long alkyl or perfluoroalkyl chains) have been attached [3–5]. The interesting feature of HMP is their ability to produce highly viscous aqueous solutions above a concentration threshold. This viscosity enhancement, much higher than the viscosity of the unmodified precursor under the same conditions, is due to the strong tendency of their hydrophobic parts to form intermolecular aggregates in aqueous solutions [6–13].

The performances of these polymers can be improved by mixing HMP with other species containing hydrophobic moieties inside their structure. The mixed associations formed in aqueous solution between stickers of associating polymers and macromolecular additives (proteins, synthetic polymers) or surfactants [14–18] can lead to a strong synergy of the viscoelastic properties [19]. The rheological behaviour depends on the mixing ratio, i.e. on the efficiency of the formed hydrophobic cross-links. HMP adsorb also on hydrophobic surfaces and can be used as stabilisers for hydrophobic particles [1,20,21], emulsions [22,23], organic liquids or membrane proteins [24] in aqueous solution.

Most of aqueous polymer solutions used in industrial applications, as thickeners to control the rheology of aqueous based fluids, are characterized by a loss of viscosity under heating. This usual feature turns out to be a major drawback in many applications carried out at high temperature or in a wide range of temperature, such as aqueous suspensions, coatings, drilling fluids and general works in deep subterranean formations. In most cases, the decrease in viscosity with temperature leads to a loss of efficiency or a lack of control

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of the process and there is a need for technological fluids which could enhance reversibly their viscosity upon heating. This property, which is opposed to gelation upon cooling described long ago with natural polymers like gelatine, has been reported initially with cellulosic derivatives (methyl, hydroxypropyl, ethyl(hydroxyethyl)) and their mixtures with ionic surfactants [25–29]. This specific property has been exemplified mainly during the last two decades with synthetic block copolymers, like poly(ethylene oxide)-*b*-poly(propylene oxide) [30–32], and then clearly rationalised with graft copolymers tailored with responsive side-chains [33–38]. Even though all these systems are chemically different, they follow the same rules of hydrophobic solvation. It corresponds to a subtle heat exchange between solute and water molecules, corresponding to rearrangements between Van der Waals forces and hydrogen bonds, but the important point is that water molecules also reduce their entropy by forming ice-clusters around the non-polar groups. As the temperature is increased, the thermal motions progressively lead to a very unfavourable situation for the water shell, which can no longer subsist. This breakdown subsequently triggers the aggregation of the hydrophobic groups. A physical network can be obtained above a critical polymer concentration (Cgel) provided that the overall solubility of the polymer chain remains strong enough to counterbalance the attractive forces generated upon heating. These systems are generally called thermoresponsive, thermo-associating or thermothickening polymers [TP]. Such polymers were developed in our group with poly(sodium acrylate) (PAA) derivatives grafted with macromolecular chains characterised by a lower critical solution temperature (LCST) in water like poly(ethylene oxide) derivatives [PEO] or poly(*N*-isopropylacrylamide) [PNIPA] [33–37].

Considering alkyl groups or LCST stickers, grafted architectures can be readily prepared and provide a very good control for aqueous formulation rheology under given environmental conditions. For instance either thermothinning or thermothickening behaviours can be obtained but problems could exist for technological applications were the main requirement is a high viscosity in the widest range of temperature.

Taking into account the possibility to couple the opposite properties triggered by hydrophobic and LCST stickers, and the potentiality of mixed aggregates formation between hetero-stickers, we define the basis of a fundamental work dedicated to network structure and viscoelastic properties induced by coupling interaction in associating polymers. This work has been developed using two different approaches taking into account the possibility to incorporate hetero-stickers into different chains (study of mixtures between HMP and TP) or into the same chain (study of double grafted copolymers: HMTP).

In the present paper, which is the first of a forthcoming series, we will describe the synthesis of associating polymers (single and double grafted architectures) and we will study their swelling behaviour in dilute solutions in order to investigate intra-chain self assemblies.

2. Experimental section

2.1. Monomers, reactives and solvents

N-Isopropylacrylamide (NIPA; Aldrich), dicyclohexylcarbodiimide (DCCI; Across), 2-aminoethanethiol hydrochloride (AET,HCl; Fluka), potassium persulfate (KPS; Prolabo), *N*-methylpyrolidone (NMP; SDS) and all organic solvents were all analytical grade reagent and used as received. Water was purified with a Milli-Q system from Millipore.

2.2. Polymer precursors

Polyacrylic acid, 35% (w/w) solution in water, was purchased from Aldrich, and freeze dried before use. Dodecyl amine (C12-amine; Fluka) was used without further purification. Two poly(ethylene oxide-*co*-propylene oxide) random copolymers of general formula: $CH_3O(CH_2CH_2O)_n(CH_2CH(CH_3)O)_mCH_2CH(CH_3)NH_2$ with different ethylene oxide and propylene oxide content where kindly supplied by Huntsman (Belgium) and used as received. According to their composition the 2 samples will be called PPO ($m>n$) and PEO ($n>m$). An amino-terminated PNIPA was prepared by telomerisation as previously reported in details [37]. The synthesis can be summarised as follows. In a three necked flask equipped with a reflux condenser, a magnetic stirrer and nitrogen feed, 10 g of NIPA (90 mmol) was dissolved in 100 mL of water and the solution was deoxygenated during 1 h with nitrogen bubbling. The initiators KPS (0.9 mmol) and AET, HCl (1.8 mmol) were separately dissolved in 10 mL of water prior to be added to the NIPA solution. The reaction was allowed to proceed at a controlled temperature of 20 °C. After 4 h, an appropriate amount of sodium hydroxide was added to neutralise the hydrochloride ions and the polymer was recovered by dialysis against pure water (membrane cut-off = 6000–8000 Da) and freeze drying. The reaction yield was 52% (Table 1).

2.3. Grafting reaction

The coupling reaction between carboxyl groups of PAA and primary amine was performed in an aprotic solvent (NMP) using DCCI as coupling agent. Similar conditions were used for the modification of PAA with different amines. In a

Table 1
Composition and average molar mass of polymer precursors

Polymer	Average number of monomer units[a]	M_n (g/mol)	Ip
PAA	(AA) = 530	50,000[b]	4–5
PNIPA	(NIPA) = 53	6000[b]	2
PPO	(PO) = 37/(EO) = 7	2500[c,d]	1.05
PEO	(PO) = 8/(EO) = 28	1800[c]	1.05

[a] Average number of monomer units and composition were obtained from M_n for homopolymers and ^1H NMR for copolymers.

[b] Molar masses were determined by SEC.

[c] Molar masses were determined by ^1H NMR.

[d] Molar masses were determined by mass spectrometry.

three-necked flask, equipped with a reflux condenser and a magnetic stirrer, PAA was dissolved in NMP for 18 h at 60 °C with an oil bath. Amino compound and DCCI were separately dissolved in NMP. The solution of amine was introduced slowly into the reaction mixture followed by a drop wise addition of DCCI solution. The reaction was allowed to proceed during 20 h at 60 °C. Then the flask was immersed in a cold water bath and the dicyclohexylurea by-product was filtered off. The copolymer was then progressively precipitated by drop wise addition of a concentrated NaOH solution (NaOH/COOH ∼ 2). The precipitate was washed several times with NMP in order to remove unreacted reactants and by-products. Last traces of NMP were removed by washing several times with methanol and diethyl ether. The polymer precipitate was filtered off and dried under vacuum.

Double grafted polymers were prepared by stepwise addition of amino-terminated LCST-polymer followed by C12 amines. In both addition steps the reaction was preceded for 20 h at 60 °C under stirring. The precipitation procedure was same as above.

Finally, all the copolymers were purified by dialysis during one week against pure water (membrane cut-off 6000–8000 Da) and freeze dried.

2.4. ^{1}H NMR

Polymer precursors and modified samples were characterised by ^{1}H NMR in D_2O and/or CD_3OD with a Brucker WP 250 spectrometer (250 MHz). The peaks of HOD and TMS were used as references for spectra obtained in deuterated water and methanol, respectively.

2.5. Size exclusion chromatography (SEC)

SEC analyses were carried out on PAA and PNIPA samples using a Waters system equipped with four Shodex OH-pak columns equilibrated at $T = 20$ °C in aqueous solution ($LiNO_3$ 0.5 mol/L). A dual detection ‘viscometry/refractometry’ allows an absolute characterisation of the molar masses after an initial calibration of the columns with PEO standards.

2.6. Differential scanning calorimetry

Phase transition of PPO and PNIPA derivatives induced by heating were studied by differential scanning calorimetry (DSC) with a microDSCIII from Setaram. Samples of approximately 0.8 mL, equilibrated with a reference filled with the same quantity of solvent, were submitted to temperature cycles between 5 and 70 °C with heating and cooling rates of 1 °C/min.

2.7. Viscometry

Intrinsic viscosities of precursors and grafted copolymers were determined by capillary viscometry using an automatic Ubbelohde viscometer (SEMATech Til). For most of the copolymers, initial stock solutions were prepared at a polymer concentration $C = 5 \times 10^{-3}$ g/mL and the experiments were carried out using two different thermodynamic conditions: (1) NaCl 0.05 mol/L at 20 °C and (2) K_2CO_3 0.3 mol/L at 30 °C.

3. Results and discussion

3.1. Synthesis of copolymers

Prior to grafting, the composition and molar mass of macromolecular precursors was determined (Table 1). The monomer composition of amino terminated polyether was obtained by ^{1}H NMR using the relative intensities of methyl and methylene protons of ethylene and propylene oxide units.

As we can see from Table 1, the two polyether samples are characterised by similar molar masses but opposite composition with 84 mol% of propylene oxide units for PPO and 77 mol% of ethylene oxide units for PEO. Due to this large difference, the two copolymers exhibit very different thermodynamic properties in water. While PEO solutions are fully soluble at all temperature (0–100 °C), a 1% (w/w) solution of PPO in water phase separates above 20 °C. Compared to polyether, amino terminated PNIPA has a broader molar mass distribution and is characterised by a higher number average molar mass. This point has to be considered for the subsequent step of grafting. As a matter of fact, by introducing the same number of grafts on a PAA backbone, the weight fraction of side-chains will be almost three times higher for PNIPA compared to polyether. For that reason we preferred to work with these three macromolecular grafts using comparable weight fraction rather than comparable number of chains.

Graft copolymers were prepared according to the classical reaction of amines with carboxylic acids in the presence of a coupling agent, dicyclohexylcarbodiimide (DCCI) (Scheme 1) following the procedure described in Section 2.

The same reaction could also be performed at high temperature in water, using a water-soluble carbodiimide [34], but in that case some heterogeneity in the graft distribution will be expected due to the low solubility of LCST and hydrophobic precursors during the reaction. By using NMP as reaction medium, it was possible to graft successively amino-terminated polymers and dodecylamine without any intermediate purification. From the composition determined by ^{1}H NMR (Table 2, Fig. 1), we can see that the grafting reaction is quantitative for most of the precursors: PPO, PEO and C12. This holds for both single grafted and double grafted copolymers and we can imagine that a one pot

$$\mathbf{P_1{-}COOH + H_2N{-}P_2 + R{-}N{=}C{=}N{-}R \xrightarrow[60^\circ C]{NMP} P_1{-}CONH{-}P2 + R{-}NH{-}CO{-}NH{-}R}$$

Scheme 1. Coupling reaction between carboxylic acids of the water-soluble backbone ($\mathbf{P}_1$) and amino terminated chains ($\mathbf{P}_2$).

Table 2
Nomenclature and composition of grafted copolymers

Copolymers	Molar composition of copolymers				Grafting yield	M_{eq} (g/mol)[a]
	PNIPA	PPO	PEO	C12		
PAA	–	–	–	–	–	94
PAA*g*10C$_{12}$	–	–	–	10	100%	108
PAA*g*PPO	–	2.7	–	–	96%	161
PAA*g*PPO*g*10C$_{12}$	–	2.9	–	11	100%/100%	182
PAA*g*PEO	–	–	4	–	100%	163
PAA*g*PEO*g*10C$_{12}$	–	–	4	10	100%/100%	178
PAA*g*PNIPA	0.4	–	–	–	35%	120
PAA*g*PNIPAM*g*10C$_{12}$	0.4	–	–	9	35%/100%	132

[a] Average molar mass per monomer unit of the main chain (PAA under Na salt form).

grafting, carried out by using two different grafts at the same time, would also give similar results as the reaction proceeds homogeneously to full conversion.

A lower grafting efficiency (35%) is nevertheless observed for PAA derivatives grafted with PNIPA. This low value can be correlated to a low functionality (lost of control during telomerisation process) or presence of ammonium ion groups (NH_3^+) of PNIPA chains. From experiments performed in our group, it was observed that NH_3^+ groups do not participate in the coupling reaction with carboxylic acid when the reaction proceeds in organic medium. From the above hypothesis, we would expect a low conversion with the single grafted PAA*g*PNIPA, if a fraction of PNIPA chains terminated by NH_3^+ groups remains unreacted after the first step. However, the addition of large amount of NH_2–C12 during the second step of the reaction would normally allow an exchange of protons between all amino groups and lead to higher grafting efficiency of PNIPA.

From Table 2, it can be seen that we get similar grafting yield (mol%) for single grafted and double grafted copolymers. This indicates that most of amino end-groups of PNIPA are under NH_2 form and consequently the low conversion observed during grafting (35%) mainly comes from the telemorisation itself [39].

Finally, since the reaction medium is homogeneous (PAA, PNIPA, PPO, PEO and C12 are readily soluble in NMP) we will assume a random distribution of the side chains. This was clearly shown with PAA*g*C12 by Iliopoulos and coworkers [39], using large amounts of C12 (20% in mol). As a conclusion of this part, we will point out that the coupling

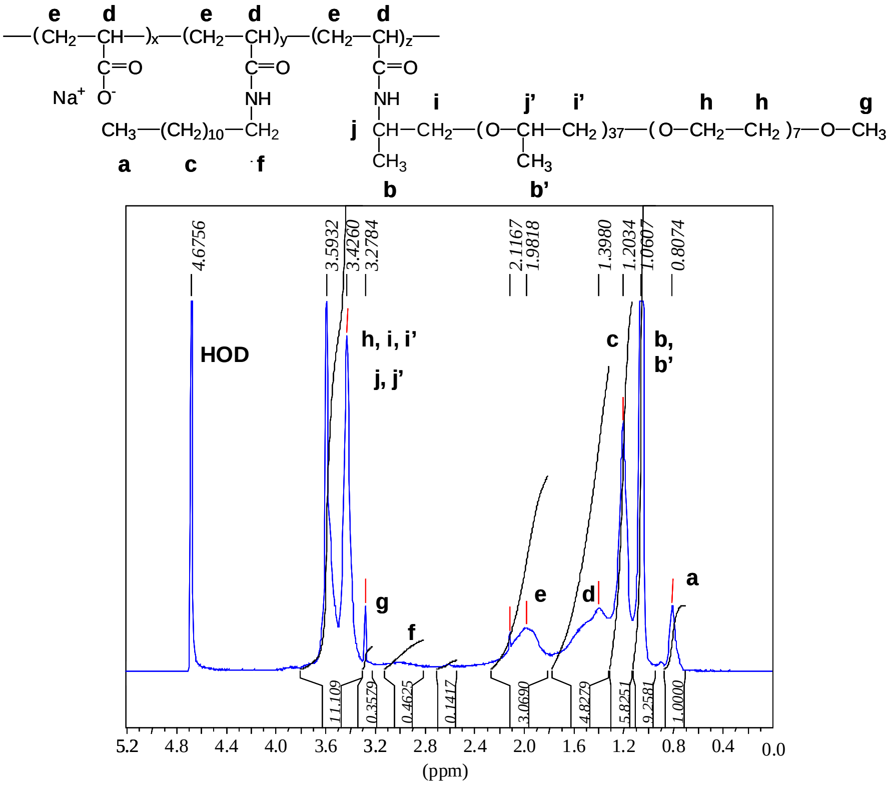

Fig. 1. ^{1}H NMR spectrum and structure of PAA*g*PPO*g*10C$_{12}$ in D_2O.

reaction involving carbodiimide agent is particularly well adapted to our initial purpose. On the basis of one backbone and four different grafts we get a homogeneous series of eight random grafted copolymers (single and double) which will be the basis of our next studies concerning self-assembling properties in aqueous media.

3.2. Dilute solution properties

Data treatment. Prior to examine the collective behaviour of copolymer in semi-dilute solution, the aim of the present work is to get a first insight into the swelling behaviour of macromolecular chains in dilute solution. For that purpose, viscosity measurements were performed on a capillary viscometer in order to get a quantitative evaluation of the hydrodynamic volume of the copolymers and to enlighten the role of different side chains on the swelling/collapse behaviour of the macromolecular structure. From a typical set of experiments, corresponding to the determination of flow times of polymer solutions at different concentrations, the dimension of the polymer and its interactions with the solvent are generally analysed by applying the Huggins relation [40]:

$$\frac{\eta_{sp}}{C}=\frac{\eta-\eta_0}{\eta_0 C}=\frac{t-t_0}{t_0 C}=[\eta]+k_H[\eta]^2C \tag{1}$$

Here, η is the viscosity of the solution, η_0 is the viscosity of the solvent, t and t_0 are the flow times measured with the capillary viscometer for the polymer solutions and the solvent, respectively, C is the polymer concentration, k_H is the Huggins coefficient and $[\eta]$ is the intrinsic viscosity. The parameter η_{sp} is called the specific viscosity and η_{sp}/C, the reduced viscosity.

If this relation applies very well to a large range of polymer/solvent/temperature conditions, there are some specific cases where it fails to describe the solution properties and cannot be used to get hydrodynamic information. This is the case for instance with polyelectrolyte aqueous solutions where the dilute solution properties obey the Rabin relation [41]:

$$\frac{\eta_{sp}}{C}\propto\frac{C}{I^{3/2}} \tag{2}$$

where I is the ionic strength of the solution.

The experimental conditions used in the present study were selected in order to avoid any strong polyelectrolyte effect. Using NaCl 0.05 mol/L or K_2CO_3 0.3 mol/L, we will assume that the total ionic strength of the solution is mainly fixed by the added salt. Under these conditions, the reduced viscosity of the polyelectrolyte chain must increase linearly with its concentration.

In the case of hydrophobically modified polyelectrolyte solutions, some examples have been reported where dilute solutions, in low salt regime, behave in a classical way and obey the Huggins and Kraemer relations [42,43]. In other cases, i.e. when Huggins and Kraemer equations fail, a linearisation of the data has been proposed on the basis of the Fedors relation. This latter has been successfully applied to macromolecular systems which display a strong concentration dependence of their hydrodynamic properties. This is the case with polyelectrolyte systems but also with associating polymers where the level of intra-chain associations can vary largely with polymer concentration [44,45].

Initially developed to describe the viscosity of Newtonian suspensions of rigid particles, Fedors has shown on the basis of a large set of experimental data that the following equation can be applied to relative viscosities ($\eta_r=\eta/\eta_0$) ranging between 1 and 100 [46]:

$$\frac{1}{2(\eta_r^{1/2}-1)}=\frac{1}{[\eta]}\left(\frac{1}{C}-\frac{1}{C_m}\right) \tag{3}$$

In this relation, the concentration parameter C_m has the same meaning as ϕ_m for particles, which is the maximum packing fraction.

On the basis of this discussion, we have applied a dual data treatment to all our copolymer solutions by using Huggins and Fedors relations (Table 3).

From a general point of view, the intrinsic viscosities obtained from the two relations are always very close even if the Fedors treatment generally gives the best fitting (especially in K_2CO_3 0.3 mol/L at $T=30$ °C). Nevertheless, the Huggins plot remains the best way to readily compare the tendency of macromolecular chains to swell or to collapse according to their primary structure (chemical composition) or to their environment. This can be observed in Figs. 2 and 3 where two sets of polymers can be easily distinguished just by taking into account the relative values of the reduced viscosity. In NaCl 0.05 mol/L at 20 °C, intrinsic viscosities are above 100 mL/g

Table 3
Analysis of viscometric data according to Huggins and Fedors relations. ($[\eta]$ in mL/g)

Polymer	NaCl 0.05 M ($T=20$ °C)			K_2CO_3 0.3 M ($T=30$ °C)			$\alpha^3_{salt}=([\eta]_1)/([\eta]_2)$
	$[\eta]_1^{Hug}$	k_{H1}	$[\eta]_1^{Fed}$	$[\eta]_2^{Hug}$	k_{H2}	$[\eta]_2^{Fed}$	
PAA	153	0.33	153	75.1	0.36	75.3	2.0
PAA*g*10C12	82.4	0.10	82.6	25	1.92	27	3.0
PAA*g*PPO	121	0.42	122	41	1.20	43	2.8
PAA*g*PPOg10C12	58.5	0.60	58.8	14.8	3.22	16.7	3.5
PAA*g*PEO	129	0.48	130	77.1	0.30	77	1.7
PAA*g*PEO*g*10C12	54.7	1.50	55.2	34.8	−0.91	35.4	1.6
PAA*g*PNIPA	124	0.36	125	72	−0.19	74	1.7
PAA*g*PNIPA*g*10C12	67.7	0.65	68.0	28,6	−0.22	29	2.3

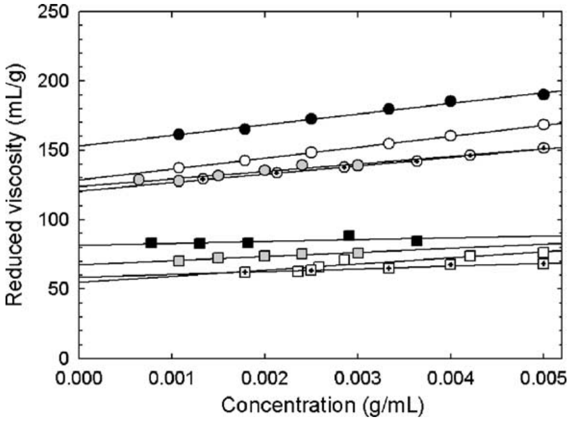

Fig. 2. Huggins plots for polymers in NaCl solution (0.05 mol/L) at $T=20$ °C. ● PAA, ⊙ PAA*g*PPO, ○ PAA*g*PEO, ● PAA*g*PNIPA; ■ PAA*g*10C12, ⊡ PAA*g*PPO*g*10C12, □ PAA*g*PEO*g*10C12, ▨ PAA*g*PNIPA*g*10C12.

for the hydrophilic series and below 100 mL/g for the hydrophobic one (Fig. 2).

In K_2CO_3 0.3 mol/L at 30 °C, a general decrease in intrinsic viscosities is observed in relation with the screening of electrostatic repulsions (Fig. 3). Two series are always clearly distinguished, one above 50 mL/g and the other one below.

Remarkably, as the PPO side-chains are above their transition threshold ($T_c=12$ °C), they self-associate and give rise to a collapse of the macromolecular structure. The other interesting feature that can be inferred from the dilute solution study is the magnitude of the fitting parameter, k_H. Huggins coefficients generally range between 0.3 and 0.5 for polymers in good and ordinary solvents, but they can be higher (>0.5) as soon as polymer–polymer interactions start to prevail in the solution. Before going further, we point out that the Huggins coefficient data must be taken with caution, because of their large uncertainty (20%), and the following discussion is thus made simple. At low salt concentration for instance (NaCl 0.05 M and $T=20$ °C; see Table 3), all the polymers of the hydrophilic series (without C12) typically show a set of k_H values between 0.3 and 0.5, as expected from their composition. In the same conditions, the hydrophobic series display higher k_H values (between 0.6 and 1.5). This could mean that hydrophobic associations already exist and that intermolecular interactions become important with increasing concentration. Note that we get a very small coefficient ($k_H\sim0.1$) in the case of PAA*g*10C12 where hydrophobic associations are also clearly expected. This very low value comes mainly from the difficulty to apply the Huggins relation in that case (the regression coefficient is below 0.85).

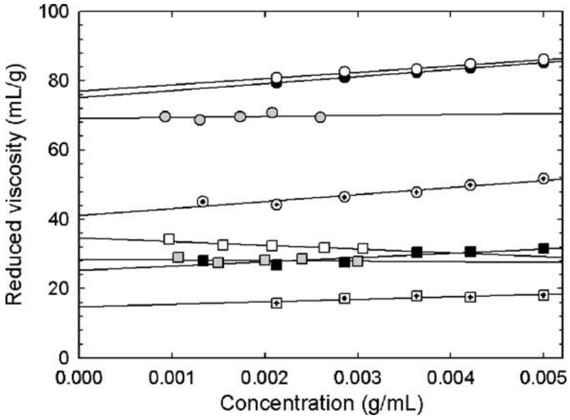

Fig. 3. Huggins plots for polymers in K_2CO_3 solution (0.3 mol/L) at $T=30$ °C. ● PAA, ⊙ PAA*g*PPO, ○ PAA*g*PEO, ● PAA*g*PNIPA. ■ PAA*g*10C12, ⊡ PAA*g*PPO*g*10C12, □ PAA*g*PEO*g*10C12, ▨ PAA*g*PNIPA*g*10C12.

At higher ionic strength and temperature (K_2CO_3 0.3 M and $T=30$ °C; see Table 3), low k_H values are again obtained for the last two non associating copolymers (PAA and PAA*g*PEO). As a matter of fact, PNIPA and PPO side-chains are now above their LCST and they are able to drive associations within copolymer chains. Concerning the potentially associating systems, we get k_H values higher than 1 for PAA*g*10C12, PAA*g*PPO and PAA*g*PPO*g*10C12, in agreement with the attractive contribution of the grafts. However, we also obtain negative values for PAA*g*PEO*g*10C12, PAA*g*NIPA and PAA*g*NIPA*g*10C12, for which a clear interpretation cannot be given at the present time. One can only suggest the formation of more and more compact polymer chain structure (due to strong intrachain interactions) causing the decrease in the reduced viscosity as concentration is raised.

In the following part of the discussion, based on the swelling behaviour of the macromolecular chains, we will use the intrinsic viscosities to describe quantitatively the specific volume of an isolated chain:

$$[\eta]\sim\frac{v}{M} \tag{4}$$

with v, the molecular volume of the swollen copolymer chain and M, its molar mass.

Discussion. In order to compare the swelling behaviour of our different copolymers in aqueous media we will start with the intrinsic viscosities determined in NaCl 0.05 mol/L at $T=20$ °C. The choice of these conditions was first dictated by the necessity to avoid strong polyelectrolyte effect which is known to infer onto the extrapolation of intrinsic viscosity at infinite dilution. This is realised by working at constant ionic strength, independently of the polymer concentration, i.e. adding salt at a moderate concentration (Eq. (2)). The second point that has to be considered is related to the solubility of macromolecular side-chains like PPO and PNIPA which are also very sensitive to the presence of salts. Following the Hoffmeister series, salts are effectively known to strongly modify the solubility of LCST polymers and generally a decrease in the critical temperature is observed by adding salt (salting out effect) [47–49]. The conditions used in the present study, NaCl 0.05 mol/L and $T=20$ °C, were selected in order to avoid any associating process with the three different macromolecular side-chains.

As we can see from Table 3, the introduction of side-chains onto the polyelectrolyte backbone gives rise to a general decrease in the intrinsic viscosities. In other words, the specific volume of the swollen chain decreases when non-ionic or hydrophobic pendant chains are incorporated inside the polyelectrolyte structure. It is well known that for a given molecular weight, a branched copolymer always has a lower hydrodynamic volume or a higher density, compared to its linear reference. Here the comparison cannot be done simply as the molecular weight of the chain increases with the grafting and consequently each polymer has a distinct molar mass. Nevertheless, as the molar mass of the grafted copolymer is always higher than the mass of the precursor, the viscosity decrease is implicitly correlated to a higher density of molecular structure (Eq. (4)). From Table 3 we can easily distinguish:

1. the 'hydrophilic derivatives', carrying PPO, PEO or PNIPA side chains, which exhibit only a small decrease in their intrinsic viscosity (around 20%) by comparison to PAA
2. the hydrophobic family, based on the 10C12 series, for which the decrease is always higher than 50%.

This qualitative comparison supports the idea that the introduction of dodecyl groups, which undergo hydrophobic association in aqueous solution, leads to the contraction or deswelling of the polymer chain. This holds for both single grafted and double grafted copolymers showing that hydrophobic domains are formed in these conditions, independently of the presence of hetero side-chains.

The second set of experiments performed in K_2CO_3 (0.3 mol/L) at 30 °C corresponds to rather different thermodynamic conditions as (1) the ionic strength is much higher, and (2) the temperature is now above the critical temperature of PPO and PNIPA grafts. As the swelling behaviour of the individual coil results from the equilibrium between its internal osmotic pressure (Π_{chain}) and the osmotic pressure of the external medium (Π_{ext}), we can use the different contributions to describe qualitatively the swelling of our copolymers:

$$\begin{aligned}\Pi_{\text{chain}} &= \Pi_{\text{m}} + \Pi_{\text{elast}} + \Pi_{\text{coul}} + \Pi_{\text{ion}} + \Pi_{\text{st}} + \Pi_{\text{graft}} \\ &= \Pi_{\text{ext}} = \Pi'_{\text{ion}} = RT\Sigma C'_{\text{i}}\end{aligned} \tag{5}$$

where Π_{m}, Π_{elast} and Π_{coul} are the respective contributions of the polyelectrolyte backbone (mixing [m], elasticity [elast] and Coulombic interactions [coul]), $\Pi_{\text{ion}} = RT\sum C_{\text{i}}$ is the contribution of the ions inside the macromolecular coil, Π_{st} is the contribution resulting from the association between the stickers, Π_{graft} is the contribution from the macromolecular grafts (depending on their solubility Π_{graft} can be described either by a mixing term or by a sticky contribution), Π'_{ion} is the contribution from electrolytes in the external medium with C_{i} and C'_{i} the free ion concentration inside and outside the chain, R is the gas constant and T is the temperature.

From Table 3 we can see that all the intrinsic viscosities decrease by increasing the ionic strength; from NaCl 0.05 M at $T = 20$ °C to K_2CO_3 0.3 M at 30 °C. The first reason of this deswelling comes from the higher screening of the electrostatic repulsions inside the polyelectrolyte chain. The Debye length (r_{D}), which is the characteristic length of the electrostatic interactions, decreases with increasing the ionic strength. Consequently, the Coulombic contribution to the osmotic pressure (Π_{coul}) that is responsible for the high extension of the polyelectrolyte chain in pure water is reduced. Here we consider that electrostatic repulsions between fixed charges of the backbone are the main ionic contribution to the overall osmotic pressure. Nevertheless, if we take into account the other ionic term, coming from the excess of ionic concentration inside the coil ($\Delta\Pi_{\text{ion}} = RT\sum(C_{\text{i}} - C'_{\text{i}}) > 0$), it goes in the same direction as Π_{coul}, $\Delta\Pi_{\text{ion}}$ decreases and the chain collapses with increasing salt concentration.

The immediate consequence for hydrophobic copolymers is the increase in the sticker's contribution which can be written under the following form [50]:

$$\Pi_{\text{st}} = -\frac{k_{\text{B}}T}{a^3}\left(\frac{h\phi_2 p}{2}\right) \tag{6}$$

with k_{B} the Boltzmann constant; a^3, the molecular volume of the solvent; h, the fraction of hydrophobic segments (nh being the total number of stickers per chain with n the total number of monomers); ϕ_2, the volume fraction of polymer and p the fraction of stickers that are associated by pairs.

The fraction of associated stickers (p) increases with increasing interaction energy between the stickers (increasing the alkyl chain length for example) but also with increasing the concentration inside the coil. This later argument is the main reason for the higher collapse of PAA*g*10C12 ($\alpha^3_{\text{salt}} = 3$) compared to PAA ($\alpha^3_{\text{salt}} = 2$) upon increasing ionic strength (the collapse coefficient (α^3_{salt}) is defined as the ratio between intrinsic viscosities determined in NaCl 0.05 M ($T = 20$ °C) and in K_2CO_3 0.3 M ($T = 30$ °C), respectively). As p increases, Π_{st} becomes more negative and favours a higher collapse state for the chain. As shown with PAA and PAA*g*10C12, the ionic strength has a strong impact on the associating behaviour by favouring attractive contributions but for the other copolymers the contribution of macromolecular side-chains (Π_{graft}) must be taken into account. When water is a 'solvent' for the side chains (from good to theta solvent), they will contribute positively to the osmotic pressure. This is the case for instance with PEO derivatives, which definitely show a lower tendency to collapse with increasing ionic strength. This is also observed with PAA*g*PEO*g*10C12 and this can be accounted mainly from the competition between hydrophobic forces that tend to reduce the size of the chain and excluded volume effects from PEO grafts that remain highly soluble in water in these conditions. In the opposite case, i.e. if the grafts are not readily soluble in water, they will act as stickers and they will contribute negatively to the swelling behaviour of the chain. This is the main reason for the strong collapse of the PAA*g*PPO sample ($\alpha^3_{\text{salt}} = 2.8$) as intra-chains associations have been triggered by increasing both ionic strength and temperature. From DSC experiments, performed in K_2CO_3 (0.3 M), it can be shown (Fig. 4) that PPO associations effectively take place at 30 °C. From the integration of the thermogram, one can estimate that at least 76% of the phase transition is over at 30 °C. If we compare to the reference value of 5.5 kJ/mol of propylene oxide unit (PO), obtained with the PPO precursor,

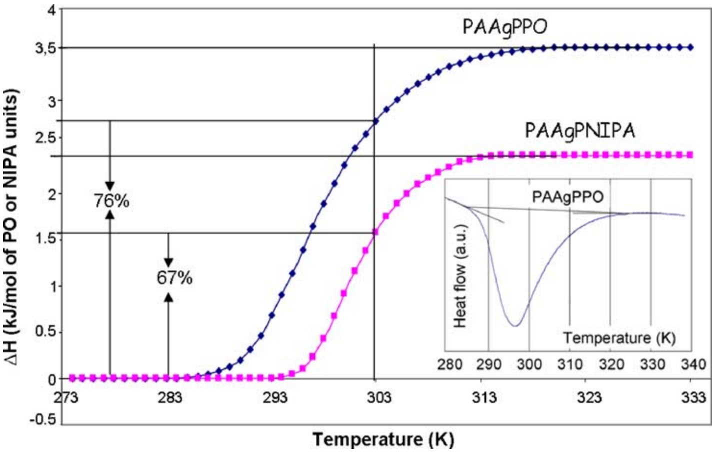

Fig. 4. Thermal analysis of PAA*g*PPO and PAA*g*PNIPA ($C_{\mathrm{PAA}}=3$ wt%) in K_2CO_3 aqueous solution (0.3 mol/L). Insert: thermogram of PAA*g*PPO.

2.8 kJ/mol of PO units means that approximately 50% of PO units in PAA*g*PPO have undergone a dehydration process at $T=30$ °C. By comparison, the yield of the phase transition is a little bit lower for the PAA*g*PNIPA solution at 30 °C (67%) and if we take a reference value of 4.5 kJ/mol of NIPA units, as obtained with the PNIPA precursor, this will correspond to a dehydration extent of 30% for PNIPA graft in these conditions. Taking into account all these specific contributions to the osmotic pressure, it is clear that the largest collapse will be obtained with PAA*g*PPO*g*10C12 ($\alpha^3_{\mathrm{salt}}=3.5$) as it combines the screening effect of the polyelectrolyte backbone, the increasing fraction *p* of dodecyl stickers participating to the associations and the new associations triggered between PPO grafts.

In spite of the LCST phase transition of PNIPA (Fig. 4), it appears that the grafting ratio of PAA-*g*-PNIPA copolymers is too low to induce a strong modification of the swelling behaviour in dilute solutions. On the basis of its primary structure (Table 2), the average number of PNIPA side-chains per backbone is approximately equal to 2. This average value means that some PAA chains carry zero or one PNIPA pendant chain, while others can bear several ones. By comparison with PAA*g*polyethers, where the average number of side-chains per PAA is around ten times higher than that of PAA*g*PNIPA, it is clear that the deswelling ability of PAA*g*PNIPA, regarding an intramolecular process between PNIPA above their LCST, will remain poorly effective. Nevertheless the aggregation behaviour of PNIPA grafts can be more easily evidenced when the swelling of the chain is reduced by additional hydrophobic interactions. Indeed, PAA*g*PNIPAg10C12 displays an intermediate deswelling behaviour ($\alpha^3_{\mathrm{salt}}=2.3$) ranging between PAA*g*PPO*g*10C12 ($\alpha^3_{\mathrm{salt}}=3.5$) and PAA*g*PEO*g*10C12 ($\alpha^3_{\mathrm{salt}}=1.6$).

A complementary interpretation of the intrinsic viscosities can be achieved by calculating the molecular volume (v) of the swollen copolymer chains, according to the following equations:

$$v=\frac{4\pi}{3}R_G^3 \tag{7}$$

with

$$R_G^3=\frac{[\eta]M_n}{6^{3/2}\Phi} \tag{8}$$

and

$$M_n=x_nM_{eq} \tag{9}$$

with R_G the radius of gyration of the macromolecule calculated from the Flory equation; ($\Phi=2.86\times10^{23}$ mol^{-1}, the Flory constant; $x_n=530$, the number average degree of polymerisation of the PAA backbone and M_{eq}, the average molar mass per repeating unit (Table 2).

The molecular volumes and the collapse ratio (α^3_{C12}) between single grafted and double grafted copolymers are reported in Table 4 for the eight copolymers considering the two environmental conditions. Molecular volumes were also plotted in Fig. 5 to make an easier comparison between each series (hydrophilic and hydrophobic), each pair of copolymers (single and double grafted) and each thermodynamic conditions.

In 0.05 M NaCl ($T=20$ °C), the comparison between PAA and PAA*g*10C12 displays that the polyelectrolyte chains deswell with a ratio of 1.6 due to the formation of intra-chain hydrophobic aggregates (Π_{st}). On the other hand, the introduction of long ‘hydrophilic’ side-chains on the backbone (PEO, PPO, PNIPA) leads, in the same conditions, to an increase in the molecular volume as expected with the swelling effect exerted by these side-chains (Π_{graft}; see also Fig. 5). The lower molecular volumes obtained for PNIPA derivatives can be explained taking into account the primary structure of the copolymers. Here we will assume in a very simple manner that hydrophilic grafts behave as free chains entrapped inside the macromolecular structure and we can write:

$$\Pi_{\mathrm{graft}}=RT\left(\frac{C_{\mathrm{graft}}}{M_{\mathrm{graft}}}+A_2C_{\mathrm{graft}}^2+A_3C_{\mathrm{graft}}^3+\dots\right) \tag{10}$$

with C_{graft}, the graft concentration inside the macromolecular coil (m_{graft}/v); M_{graft}, the number average molar mass of the grafts and A_2, A_3 the second and third virial coefficients.

Table 4
Molecular volumes (v) of the swollen chain and deswelling ratios between single grafted and double grafted copolymers for different environmental conditions

Polymer	M_n (g/mol)	0.05 M NaCl/$T=20$ °C		0.3 M K_2CO_3/$T=30$ °C	
		v (nm^3)	$\alpha^3_{C12}=(v_x)/(v_{x,C12})$	v (nm^3)	$\alpha^3_{C12}=(v_x)/(v_{x,C12})$
PAA	50 000	7600	1.6	4000	2.5
PAA*g*10C12	57 500	4800		1600	
PAA*g*PPO	85 500	10 400	1.8	3700	2.2
PAA*g*PPO*g*10C12	96 500	5700		1700	
PAA*g*PEO	86 400	11 200	2.1	6600	2
PAA*g*PEO*g*10C12	94 300	5200		3300	
PAA*g*PNIPA	63 600	7900	1.7	4700	2.3
PAA*g*PNIPA*g*10C12	70 000	4700		2000	

From the composition of the copolymers (M_{eq}) given in Table 2, we can estimate that the weight fraction of PNIPA in the copolymer ($\sim m_{graft}$) is two times lower than the concentration of PEO or PPO: 21% against 42%. It means that for a given volume of the macromolecular chain (V_{coil}), the absolute concentration C_{graft} will be also two times lower for the PNIPA derivative. Considering that the molar mass of PNIPA grafts is approximately three times higher than the masses of PEO and PPO (Table 1), this leads to the fact that the first virial coefficient in the equation (10) is six times lower for PNIPA derivatives compared to PEO and PPO ones. This simple calculation can be used to explain why both PEO and PPO derivatives have similar molecular volumes at low ionic strength (Fig. 5). Of course higher values are expected for PEO derivatives as the PEO molar mass is slightly lower than the mass of PPO and mainly because water is a better solvent for PEO compared to PPO in these conditions (higher values for the second virial coefficient). Similarly, the fact that at low ionic strength (0.05 M NaCl, $T=20$ °C) hydrophilic and hydrophobic PNIPA derivatives have similar molecular volumes compared to PAA and PAA*g*10C12, respectively (Fig. 5), can be attributed to the very low contribution of Π_{graft} in these conditions.

If we compare now the double grafted copolymers, containing both hydrophilic and hydrophobic stickers, the net result of the competition at low salt concentration is a strong collapse of the macromolecular structure, showing that hydrophobic attractive forces dominate the swelling behaviour of the macromolecular chain. For the whole series, the collapse coefficients are comprised between 1.6 and 2.1 with the lowest one observed for the couple PAA and PAA*g*10C12.

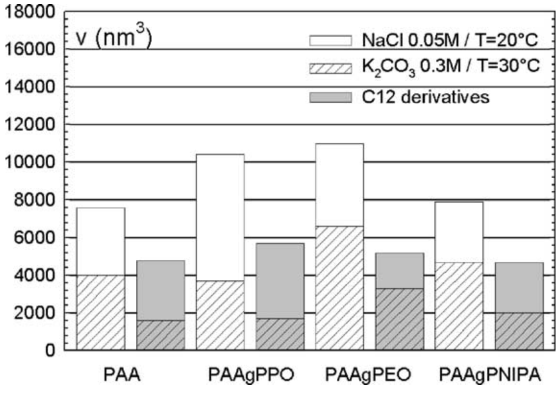

Fig. 5. Comparison between molecular volumes of copolymer chains as a function of their chemical structure and according to the environmental conditions.

In K_2CO_3 0.3 M at $T=30$ °C, similar behaviours are observed with higher collapse coefficients: $\alpha^3_{C12}=2.0$–2.5. As previously reported, the higher collapse of the copolymers chains in K_2CO_3 0.3 M ($T=30$ °C) results from a lower contribution of electrostatic repulsions to the osmotic pressure of the macromolecular coil and consequently to a higher efficiency of hydrophobic clustering. Once again, the data plotted in Fig. 5 enlighten the strong collapse of PAA*g*PPO derivatives due to the aggregation process of PPO driven by salting out. The comparisons between (1) PAA*g*PPO and PAA and (2) PAA*g*PPO*g*10C12 and PAA*g*10C12, clearly show that the molecular volumes remain roughly independent of the PPO grafting while there is a 70% increase in the molecular weight (Table 2). It means that PPO strongly aggregate inside the polymer chain, but we have not enough information to conclude about the structure of the aggregates: either segregated domains (PPO on one side and C12 on the other side) or mixed aggregates. By comparison, hydrophilic grafts like PEO maintained a higher level of swelling, in both hydrophilic and hydrophobic derivatives, due to the positive contribution of PEO grafts to the osmotic pressure.

4. Conclusions

The purpose of this work was to prepare a homogeneous series of graft copolymers containing hydrophilic, LCST and/or hydrophobic side chains. Starting with a poly(acrylic acid) backbone, a carbodiimide activation was used to condense the terminal amino group of the different grafts onto the carboxylic groups of the PAA. Two homologous series of well-defined copolymers were obtained following the concept of single grafted and double grafted copolymers. Using DSC, we show that PPO and PNIPA side chains are able to trigger thermoassociating properties around room temperature in response to an entropically driven process of dewatering. All the polymers were carefully studied in dilute solutions in order to investigate their ability to swell or to collapse according to their structure or their environment. The introduction of hydrophilic groups inside the poly(sodium acrylate) backbone is responsible for an increase in the hydrodynamic volume of the macromolecular chain in relation with an excluded volume effect exerted by these side chains. By comparison a deswelling of the macromolecular structure is induced by the aggregation of hydrophobic stickers. The collapse is even stronger when the electrostatic repulsions inside the polyelectrolyte chain are weakened by increasing the ionic strength. In the specific case of PPO derivatives which are both thermo- and iono-responsive, the nanoscale phase transition of the LCST grafts gives rise to a strong collapse of the structure evidencing the formation of intra-molecular associations. In the course of this study, it is possible to identify qualitatively the participation of the different side chains to the swelling behaviour of the macromolecule but no evidence is clearly shown for some synergy mechanism between heterografts. Starting with this first analysis on the dilute solution properties of single and double grafted copolymers, we will follow in the forthcoming papers to describe the structure and the viscoelastic behaviour of the same copolymers in semi dilute solutions.

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