Chapter

pH Dependence of Acrylate-Derivative Polyelectrolyte Properties

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Abstract

There are many polymers formed of acrylate monomers in existence. Here we interrogate four commonly-used examples and study how their solution properties are pH dependent, or how their state of ionisation can affect their solution properties. Poly(acrylic acid) and poly(methacrylic acid) are both polyelectrolytes, with ionisable functional groups that make them stimuli responsive, changing their hydrodynamic volume. Poly(acrylamide) is a mass-produced material used in a variety of industrial applications, often with an anionic and cationic co-monomer, which dictates both its efficacy and impact on the environment. Poly(*N*-isopropyl acrylamide) is a thermally responsive material with applications in smart bioengineering. In solution, these materials can interact with each other due to competing hydrogen bonding interactions. However, this interpolymer complexation is dependent on both the ionisation, and the conformational state, of the polymers involved. This review focuses on the results from fluorescence tagging and turbidimetric techniques.

Keywords: poly(acrylic acid), poly(methacrylic acid), poly(acrylamide), poly(*N*-isopropylacrylamide), stimuli responsive, interpolymer complexation, hydrodynamic volume, solution properties

1. Introduction

A common feature of the many polymer systems formed from acrylate monomers is their hydrophilicity; apparent either from their increased absorbency, wettability or increased solubility. Whilst the latter is often overlooked in materials science, it is of vital importance to a range of industries, as a multitude of polyacrylates form vital components in commercial products too varied to list, but including dispersants, adhesives, emulsifiers, lubricants, flocculants, thickeners, surfactants, sensors, delivery agents, coatings, chromatographic phases, grouting, passivation and many more. As of 2018, the multi-million tonne polyacrylate global market is still rising with an annual growth greater than 6% [1]. Research over the last 20 years into controlled radical polymerisation, and copolymerisation, has provided increased insight into the distinct properties of these materials. However, even 50 years after the initial patenting of poly(acrylic acid) [2], new discoveries about its fundamental properties are still being made [3].

In solution many, but not all, acrylate copolymers act as polyelectrolytes, containing ionisable repeat units; and thus show some form of stimuli-response to pH.

The solution forces that govern these properties are the same that give function to biological macromolecules (i.e., peptides, proteins, DNA) and so many polyelectrolytes have been used as simple models for these more complex systems. However, due to their applications are so widespread and varied, it is essential to any chemist or engineer working with these sensitive materials to acquire some understanding of the need to control their pH.

Depending on the nature of these ionisable repeat units, a polymer can be classified as a 'weak' or 'strong' polyelectrolyte, governed by the pK_a of the ionisable groups. As samples containing carboxylic acid repeat units dissociate relatively easily, they fall into the former category. The chemical structure of ionisation (or dissociation/neutralisation) is thus:

$$RCOOH \rightleftharpoons RCOO^- + H^+ \quad (1)$$

and the dissociation constant (α) can be described by the Henderson-Hasselbalch equation

$$\alpha = \left([X] + [H^+] - [OH^-]\right)/[RCOOH] \quad (2)$$

$$pH = pK_a + \log\{\alpha/(1-\alpha)\} \quad (3)$$

where X is the ionising (titrating) species and pK_a the dissociation constant; the pH at which 50% of the carboxylic groups have been ionised. However, for a polyacid, this is a more contentious issue than studying small molecules due to each acid group is affected by the presence of neighbouring repeat units, which thus modify their titration behaviour. In general, the first COOH group on a polymer backbone shows a similar pK_a to a small molecule analogue. However, as the polymer chain becomes increasingly ionised, the building negative charge constrains further deprotonation, and the pK_a value alters with increasing pH. In this behaviour, particularly polymeric electrolytes show divergent behaviour from small molecules, and Katchalksy and Spitnik proposed a revision to the Henderson Hasselbalch Equation [4].

$$pH = pK_a + n\log\{\alpha/(1-\alpha)\} \quad (4)$$

where n is a constant dependent on the ionic strength of the solution and the strength of the polyacid. In a stationary solution, this plot should produce a straight line (slope n, intercept pK_a). However, this is rarely observed, particularly in aqueous solutions, and this was the first indication researchers had that many polymeric macromolecules undergo a conformational rearrangement on the nanoscale in response to chemical ionization [4, 5]. Over the years, this has proven fertile ground for research, with poly(carboxylic acid)s receiving particular attention in the literature as they are excellent, chemically distinct, model systems [3, 4, 5–13]. However, even non-responsive systems, such as poly(acrylamide), have been found to demonstrate responsible macromolecular behaviour in the presence of corresponding polymer systems *via* a process of interpolymer complex formation [14]. Many polyacrylates engage in hydrogen bond driven complex interactions. The field has proven to be extremely complex due to the multitude of competing factors that affect this often weak, almost always labile, interface.

This chapter will discuss recent advances in the study of pH dependent polyacrylate solution behaviour, examining our improvements in understanding of

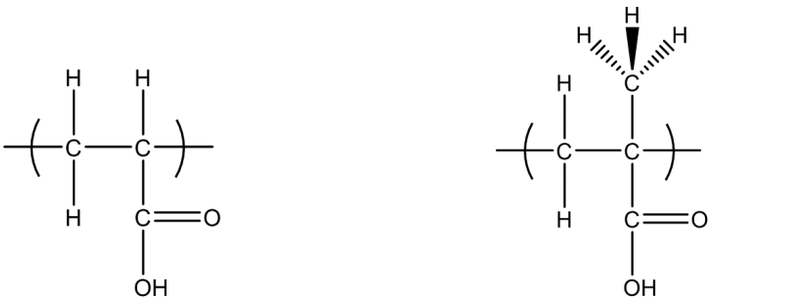
weak polyelectrolyte systems. Critically this review limits itself to studies of linear polymer systems, as the properties of branched, or crosslinked, macromolecules are fundamentally different [15, 16] and warrant further, separate discussion.

2. Poly(carboxylic acids)

The two most comprehensively studied synthetic poly(carboxylic acid)s within the literature are poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) respectively. Both contain a carboxylic acid repeat unit that dissociated to form a negatively charged anion in low pH aqueous solutions. The additional methyl group on the methacrylic acid functional group gives PMAA a degree of amphiphilic behaviour [17] depending on the degree of ionisation (**Figure 1**).

This additional hydrophobicity dominates the solution properties of PMAA, leading to the aforementioned 'anomalous' Henderson Hasselbalch titration behaviour [4, 5, 7, 9], whilst PAA has long been considered a more 'ideal' system [18] as it does not undergo as dramatic a macroscopic switch. As the carboxylic acid group can only be classed as hydrophilic when the functional monomer is protonated, PMAA undergoes a rapid swelling as the pH is increased, becoming an entirely hydrophobic material with increasing anionic charge along the backbone. Extensive investigations have been carried out into its behaviour using diverse methods and techniques: pontentiometry [4, 5, 7, 10, 19], viscometry [8, 11], Raman spectroscopy [20], scattering methods [21–23] and fluorescence probe interrogation techniques [3, 24–26]. The combined research has shown that PMAA undergoes a dramatic conformational change between pH 4 and 6, (corresponding to an α (degree of ionisation) between 0.1 and 0.3), whilst PAA adopts a relatively smooth swelling process in the same pH range (initiating at the same degree of ionisation). In acidic media, due to the increased hydrophobicity, PMAA adopts a globular, contracted structure designed to minimise unfavourable interactions between the hydrophobic backbone and side chain and the aqueous solution, whilst PAA has been described as a random, statistical coil [6, 7, 9]. The PMAA shows significantly increased compaction due to the hydrophobic methyl backbone [8, 13, 22, 24–29], that has been shown to induce *hypercoiling* [8]. This has two net effects—increased hydrophobic density gives it both greater solubilisation potential but at the cost of reduced solubility and mobility.

As the degree of ionisation is increased from pH 4 to 6 the PMAA anionic units begin populating the macromolecule backbone, resulting in a transition between pH 5 and 6 where repulsive units between these charges initiate a macroscopic switch from the compact to the water swollen (described in multiple places as 'rod like' [30, 31]) state. Due to the increased initial compaction in PMAA, this



Poly(acrylic acid), PAA Poly(methacrylic acid), PMAA

Figure 1.
Polyacid chemical structures.

macromolecular swelling results in dramatically changed properties between the compact/swollen polymer. Compared to this, the equivalent deprotonation and subsequent anionic charge drive PAA to adopt an extended state with a relatively smooth transition, with only small changes to polymer physical properties save additional anionic potential. These conformational responses to external stimuli can be viewed as 'smart behaviour' and have led to the incorporation of acrylic acid and methacrylic acid monomers being incorporated into a range of copolymer systems to act as triggers and solvating groups in a range of applications.

Due to the increased compaction, and hydrophobicity, of its globular state, PMAA can solubilise low molar mass organic compounds in solution [12, 17, 32], which is a property not shared by PAA [17, 32, 33]. This is particularly evidenced by the fluorescence emission vibrational fine structure of the aromatic label pyrene. The pyrene excited state emits multiple emission bands, and the relative intensity of bands 1 and 3 vary with different solvents, thus when dispersed in a solution it can give an indication of system polarity [34, 35]. For example, the I_3/I_1 ratio is known to vary between 0.55 (water) and 1.7 (n-pentane) [26]. This feature has been used in the study of many polymer systems, and commonly used by spectroscopists to study macromolecular aggregate structures such as colloids [36], microemulsions [37], micelles [38] and microgels [39, 40]. For example when a 10^{-6} M solution of pyrene was dispersed in an aqueous solution of PAA, the I_3/I_1 ratio did not shift from ≈0.55 between pH 3 and 10, identical to the ratio seen for a dispersion in water. This reflects the fact that any interaction between the fluorophore and the polymer does not alter the microenvironment of the label, and confirms the existence of PAA in a water-swollen conformation across the entire pH range. In PMAA at low pH, however, a I_3/I_1 ratio of 1.1 is commonly observed [12], indicating the compact hypercoiled polymer provides hydrophobic shielding from the aqueous solvent. When the pH of pyrene/PMAA solution is increased, this ratio begins to decrease at pH 5, indicating the conformational rearrangement of the polymer, until at pH 6 the probe is released into the solution, returning the fluorescence emission ratio to the state seen in both pure water and PAA. This experiment confirms both the increased solubilisation potential of PMAA over PAA and also the fact that the transition occurs over a broad pH range.

However, the electrostatic potential of these polyelectrolytes cannot be so simply described as indicating that the swollen/collapsed state is neutral/charged as there is an evident near neighbour effect present in polymers that is not seen in comparative small molecule systems [41]. This has been evidenced by the different acid dissociation titration behaviours seen in PMAA when comparing different polymer tacticities [42]. In dilute solutions intrachain interactions across the macromolecule tend to dominate its properties—the molecule can be considered a single long chain surrounded by counter ions, and their solution properties are thus governed by their corresponding electrostatic interactions, which are well described by a range of mathematical theories [43, 44]. To summarise: due to electrostatic repulsion ionisation of acrylate polyelectrolytes occurs over a much wider pH range than observed in the equivalent small molecule, and at the 'stated' pK_a only a fractional ionisation of repeat units will carry a negative charge. For example, potentiometric titrations of PAA found that, at pH 4.5 (pK_a of acrylic acid and the point at which conformational change will occur) only 1/10th of the acrylate repeat units in the polymer will carry this fractional charge [3, 45]. The polymer will continue to ionise up to pH 11 with no further polymer swelling observed despite increasing electrostatic potential of the system. Therefore, it is inappropriate to suggest that the conformational change is driven purely by electrostatic potential, as if this was solely the case further rearrangements at greater degrees of ionisation would be observed (**Figure 2**).

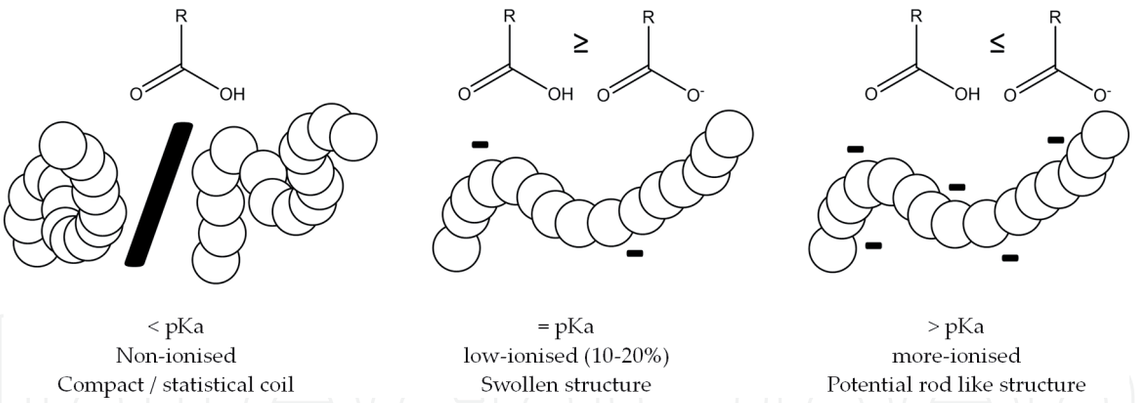


Figure 2.
Conformation of polyacid with different degrees of ionisation.

More recent data indicates that the length scale of the chain plays a role in this transition. For instance, whilst in 0.1 M NaCl the hydrodynamic radii of PAA scales with molar mass [46] the conformational rearrangement of the chai non ionisation in low ionic strength liquids only occurs above a known molar mass lower limit [3]. Current results suggest this is a salt dependent phenomenon [41, 47] and has not been observed in PMAA (although increasing polymer size does slow the kinetics of polymer reconfiguration [27]). As such differences in behaviour between low and high molar mass PAA materials have been observed, such as stark changes in the polymer behaviour at oil-water interfaces [27, 48].

3. Poly(acrylamides)

Not all polyacrylates demonstrate electrolyte properties, and one of the most common non-ionisable acrylate materials produced today is acrylamide copolymers. This chapter concerns itself specifically with two specific materials of particular interest with divergent properties, although there are a range of further examples. These polymers are poly(acrylamide) (PAM) and the hydrophobically modified poly(*N*-isopropylacrylamide) (PNIPAM), whose properties are driven by the additional hydrophobic groups along the polymer side chain. As such one is widely used as an inexpensive, mass-market commodity whilst the other is a very heavily investigated [40, 49], high value material with particular interest in its biomedical applications [50] (**Figure 3**).

Random copolymers of acrylamide (both anionic, cationic and neutrally charged) have been extensively used in the water industry for many years [51–54]. They are extensively employed to remove dissolved organic matter (DOM) for water clarification purposes. Flocculation of fine particles can occur *via* several mechanisms including polymer bridging, charge neutralisation, polymer-particle complex formation and depletion flocculation; often a combination of several of these processes [55]. Binding in poly(acrylamide) is primarily by hydrogen bonding [56], although copolymerised sections may also assist with electrostatic interaction or ion binding. In a sufficiently long polymer chain, there are many potential binding sites, and once sufficient repeat units along a single polymer chain have adhered to a particle surface, the adsorption is often considered irreversible despite the fact each individual binding site is acting in an equilibrium [53]. Once a polymer has adhered to a particle, it can be divided into three segments: *trains* (adhered to the particle surface), *loops* (that extend from the surface) and *tails* (which project into the solution). The speed by which the polymer shifts is difficult to assess but an

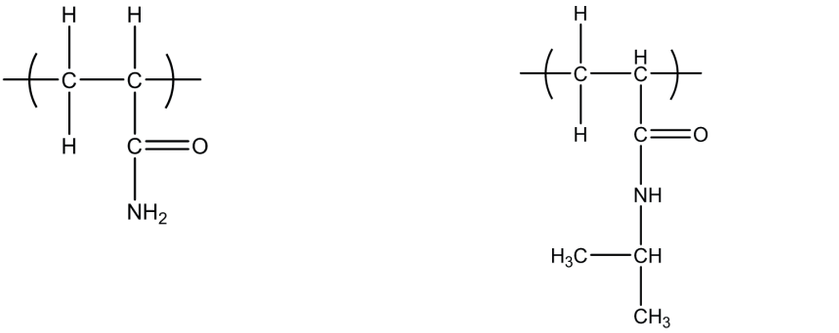


Figure 3.
Polyacylamide chemical structures.

important factor in flocculation kinetics [53]. Following the adhesion of polymer chain of sufficient length for a loop or tail to extend into the solvent, secondary attachment to secondary particles can occur in a process known as 'polymer bridging'. Polymer chains adsorbed on the particle surfaces via only a few points of attachment leave the majority of the chain in solution whilst increasing adsorption onto the particle to saturation reduces the flocculation potential of the polymer. Bridging can be impacted by both the charge density and the molecular weight of the polymer [55] (**Figure 4**).

Polyacrylamide is used in a range of other scenarios including erosion control [51, 57–59], medical implants [60–63], and reduction of water seepage via increasing aqueous viscosity to both stabilise soil and dust prevention [51]. Poly(acrylamide) was one of the first polymers used to reduce soil losses in furrow irrigation [64] and the polymer has been sold commercially for this purpose since at least 1995 [51]. Large quantities of this material are therefore escaping into the environment [59, 65] and a body of research is being built up regarding its effect on the ecosystem [66]. Generally, the polymer is considered non-toxic, with most concerns around its use arising due to its close association from the potent neurotoxin monomer from which it is formed. Since Swedish researchers discovered that acrylamide can be found in heated foodstuffs [67–72], there has been low level public concern about the use of polyacrylamides in a range of industries.

However, studies of polyelectrolyte flocculants of all types have been carried out and consistently poly(acrylamide) is identified as being the primary 'toxicant' [66]. Within much of the poly(acrylamide) literature, there has been a lot of emphasis placed on the toxicity of the monomer, resulting in studies discounting the effects of the polymer and only focusing on residual monomer spread [65]. However, some studies have shown that poly(acrylamide) is unlikely to degrade into residual monomers, or any other toxic compounds [73], and this has only been observed under specific harsh conditions [74]. Therefore, a complete study of the environmental impact of these polymers should include the raw polymeric product.

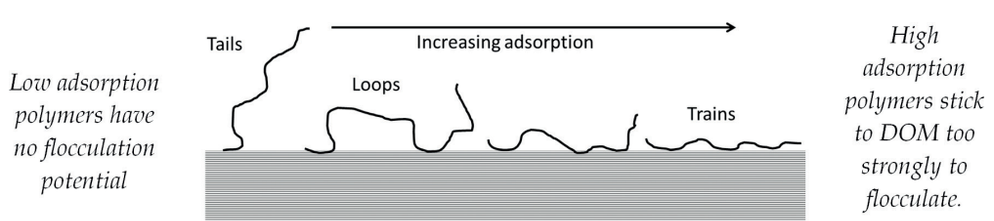
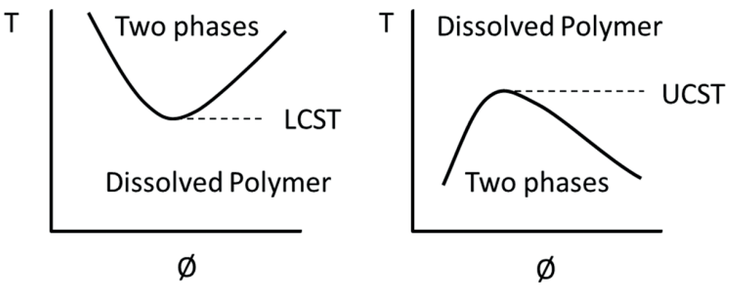


Figure 4.
Increasing polymer adsorption to surfaces.

Testing of poly(acrylamide) interaction with the gill tissues of several aquatic species including fish [66, 73, 75–77], crustaceans [66, 73, 77], algae [66, 77] and insects [77] have been carried out. In many studies of adult fish, the anionic and non-ionic form of the poly(acrylamide) cause only low levels of damage to the fish, with effects increasing at higher concentrations [75]. However, sustained exposure of organisms over a 40 day period has shown that low levels of these polymers are intrinsically toxic to almost all aquatic fauna [73]. Environmental exposure is unlikely to be sustained over long periods due to the polymer desorption to organic matter but few studies have been undertaken into the metabolic rate at which they are removed from living organisms. Even in tests where fish survival was not impacted, the general activity and swimming behaviour of the fish were sub normal [76]. Conversely the cationic form of the polymer is known to be far more toxic, causing pathological issues at sub mg ml^{-1} concentrations, as the polymer builds up on negatively charged gill surfaces [75, 77]. Reduced gill functionality impairs oxygen uptake in the fish and results in death. Further studies have shown that polyelectrolytes can cause adverse changes in fish organ cells (liver and kidneys) [73], decrease animal locomotion and greatly increase respiratory rate. This suggests that the presence of dissolved flocculants may not be lethally toxic but suggests it is capable of causing the fish elevated levels of distress. In invertebrates, their mechanical action was reduced as polyelectrolytes adsorbed onto their body surfaces, reducing their vital functions [73], and again the cationic form of the polymer is far more toxic than the anionic form. [77] In microcosms tests, it has been shown that high polyelectrolyte concentration can reduce algal growth [66, 77]. This in turn can increase the potential toxicity of the polymer as the algae acts as a neutralising agent towards the polymer. To algae, even the anionic and non-ionic polymer is toxic, negatively affecting both cell growth and O_2 production [73]. It has been observed that addition of combinations of both anionic and cationic polymer can reduce toxicity [77] and several patents have been issued suggesting that anionic polymers can be used to detoxify cationic polyelectrolytes [78, 79]. In conclusion, the discrepancy between anionic and cationic polymers in regard to aquatic toxicity must be considered in the application of these polymers [75, 77]. The cationic form of the polymer is regarded as generally more toxic but the anionic form has also been shown to cause chronic, sub-lethal responses even at low concentrations [66].

Although it has some larger applications, PNIPAM is not produced or utilised in such great quantities. It is mainly of interest due to a thermally induced conformation the polymer exhibits at 32°C, caused by the hydrophobic isopropyl groups [49]. This 'smart' response has led to great interest in the polymer, both to understand its properties and apply them in a range of fields, specifically in Bioengineering [50]. In essence, the polymer has a lower critical solution temperature (LCST), a conformational change that occurs *via* a two stage process. Firstly, the polymer has an intramolecular collapse, where individual chains contract in upon themselves as they break hydrogen bonds with the aqueous solution, followed by a secondary event of intramolecular aggregation of the collapsed coils [80]. This event is triggered by the increasing entropic cost at high temperature of the restricted water that solubilises the dissolved polymer chains below the LCST. The event has some hysteresis between heating and cooling radii of gyration [81], governed by two intermediate states that give PNIPAM four potential conformations: globule, molten globule crumpled coil and coil [82]. During the collapse the globular state dispenses approximately 34% of the water molecules [82], meaning that although this is a desolvation event leading to an insoluble material, collapsed PNIPAM can never be described as a hydrophobic system (**Figure 5**) [49].



Lower critical solution temperature (LCST)
Entropic factors separate polymers from solution

Upper critical solution temperature (UCST)
Are only soluble above a specific temperature

Figure 5.
Typical thermoresponsive properties of polymers [83]: (temperature (T) vs. volume fraction (Ø)).

The LCST of PNIPAM can be affected by the addition of hydrophobic or hydrophilic end groups [84], or the molecular weight and concentration of the sample [85]. Due to the LCST is reasonably close to body temperature, there has been much work to manipulate PNIPAM to act as a drug-delivery agent or trigger or apply it in other bio-engineering circumstances [86, 87].

4. Acrylate interpolymer complexes

Interactions between multiple polymers in a formulation are almost inevitable, and there has been plenty of studies of specific driving factors undertaken over the last 50 years to build a strong picture of inter-polymer interactions. This phase separation phenomena is observed in even the most dilute solutions, as it is driven by a mixture of electrostatic, hydrogen bonding and hydrophobic interactions, all dependent on pH, salt concentration and temperature [88, 89]. To our knowledge this type of complex was first patented in 1966 [90], with much of the following fundamental measurements carried out over the following decades [14, 91–94]. Since then, the system has been described as a *laddered* sequences of bonds between the molecules, occasionally interrupted with *loop* defects [95], an evolution similar to the model previously described of polymer adhesion to surfaces. This theory originally posed that the polymers will form rigid, static structures due to repeated hydrogen-bonding across molecules. More recent studies have put less emphasis on the polymer rigidity and have given an alternative description of these repeated labile interactions more as *ribbons* (i.e., two flexible materials that can slide over each other).

The interactions between PAA and PAM are one of the more studied systems of interpolymer complex formation (IPC) [93, 96–101], and in both solution and solid state the interaction has been shown to be pH dependant [14, 96]. Mixed solutions of PAA and PAM form a turbid solution that precipitates when cooled [97]. This phase separation follows the formation of complexes between PAA and PAM that varies in structure depending on the concentration, medium and the ionisation constant [97]. For complexes between PAA and a proton-acceptor polymer it has been shown that IPCs will only form below a critical value of pH (pH_{crit}) [14, 99], the structure dependent point above which any partial neutralisation of the poly-acid inhibits complex formation [14, 100].

Early work within this field required high molecular weight materials to detect complex formation [99, 102], however, modern instrumentation has facilitated detection of smaller complexes down at the parts per million loading level [103]. The structure of the resultant IPC (whether in a gel or a compact solvated complex)

depends on the relative molecular weight of complexing partners, [104] but as this is a multivalent effect of repeated binding sites, larger molecular weight materials demonstrate stronger interactions. Furthermore, it has been indicated that very large molecular weight polyacids have been seen to raise pH_{crit} [93].

When dissolved in high ionisation solutions, both polymers have rapid segmental motion, existing as random polymeric coils. If the solution ionisation is decreased, this deprotonates the acidic polyelectrolytes and reduces its affinity for inter-polymer complexation. This occurs as can now form both intramolecular H-bonds internally across the chain backbone or intermolecularly forming H-bonds with other polymers [105], leading to a rigid polymer mixture with restricted chain motions. PAA forms stronger complexes to PAM than some other polymers (i.e., poly(ethylene oxide) or poly(vinyl acetate)) due to additional ion-dipole interaction of the partially protonated amide groups and the C═O dipoles of PAA [106]. In ambient conditions the peak aqueous interaction between PAA and PAM occurs ≈ pH 2.69 [107] but this is affected by many environmental factors including temperature [89, 101], ionic strength [93, 107, 108] and the addition of inorganic binders [99]. The complex polymer/polymer/solvent ratio of interactions is temperature sensitive causing PAM-PAA copolymers to become upper-critical solution temperature materials (an inversion of the LCST seen in PNIPAM where they become only soluble above a specific temperature [87]). These combined external factors deteriorate the thermodynamic quality of the solvent, strengthening polymer-polymer interactions by weakening polymer-water solvation [109]. However, below pH_{crit}, only small portions of the PAM form into 'multimacroion clusters', indicating that in an equivalent system with 1:1 acid/acrylamide repeat units, a large percentage of acrylamide will be free in solution unbound to PAA [110]. This was the first result of several which have cast doubt on the ladder model, and computational modelling software of polymer/polymer ionic interactions has proposed a range of complexing structures ranging from ladders to scrambled egg structures [111]. Further experimental evidence has shown that a PAA coil does not unwind or swell on addition of a PAM polymer but potentially contracts into a smaller co-globule [112], and an explanation for this can be found when considering the difference between the pH_{crit} of IPC formation and pK_a of PAA conformational change.

Other acrylate materials, such as PNIPAM, demonstrate similar responses to polyacids, and exhibit their own IPC potential [113]. Whilst PAM-PAA interactions are dominant at lower temperatures, PAA-PNIPAM show increased interactions at high temperatures, indicating that the complex formation is driven by hydrophobic interactions not seen in the base acrylamide structure [114]. Studies using dissolved pyrene indicated these lead to stronger interactions between PAA and PNIPAM than PAA-PAM [115, 116]. Furthermore, the hydrophobic isopropyl side chain causes PNIPAM to alter its response to ionic strength. Whereas PAM-PAA complexes are strengthened by increasing ionic strength, PNIPAM complexes show decreased critical pH reducing their bond forming potential [109]. As the initial critical pH for IPC formation was larger than 3, Khutoryanskiy theorised that the increasing ionic strength partially dissociates the polyacid. As only non-ionised carboxylic groups are able to form hydrogen bonds, this impedes IPC formation and reduces the pK_a.

For PAA-PAM, pH_{crit} was found to be 2.7, whilst for increasing hydrophobic additions to the acrylamide unit (poly(ethyl acrylamide), poly(dimethyl acrylamide), poly(diethyl acrylamide), the pH_{crit} was found to increase to 3, 4, 5 respectively [14]. It is interesting to note that the most hydrophilic acrylamide polymers (including a hydrophilic-functionalised poly(hydroxyl ethyl acrylamide)) show lower pH_{crit}, indicating that their IPC with the polyacid are less tolerant of deprotonation. The PAA-PAM complex appears to separate when the first acid repeat unit

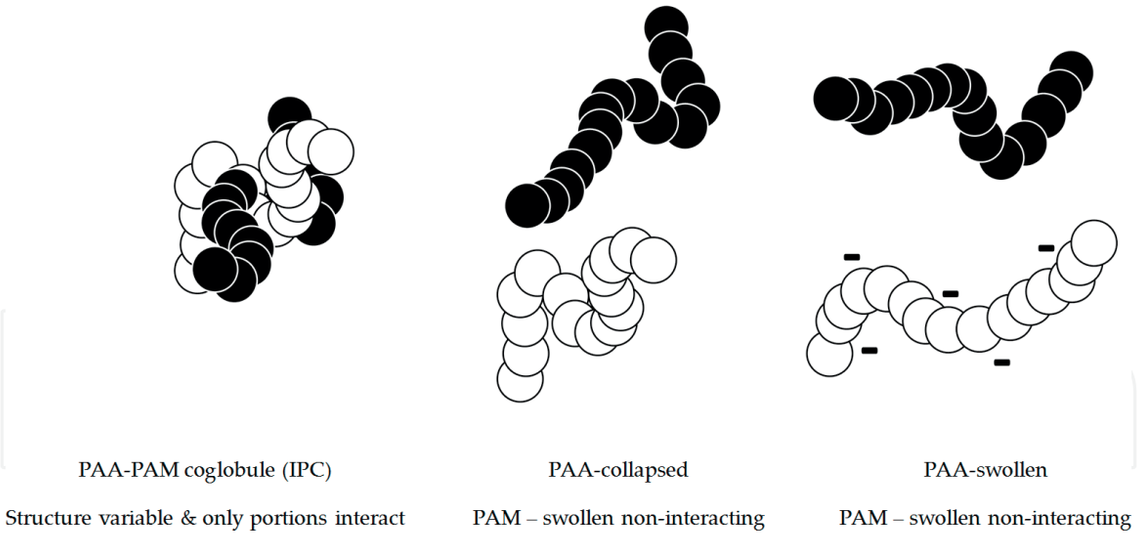


Figure 6.
Three conformational states of PAA-PAM in mixed solutions.

along the chain is deprotonated whilst more hydrophobically modified polymers are more tolerant to partial ionisation when complexing with PAA. Computational modelling of the solvation energy of each repeat unit shows a clear correlation between solvation potential and pH_{crit} [14].

Clearly the polyacid dictates the potential of IPC with receptive polymers [96], and in this mind, it is worth revisiting the PAA-PAM IPC structure. As the pK_a of the PAA is higher than pH_{crit}, it will be 'non-swollen' before it encounters a complexing partner. Early literature in the subject, comparing the supposed 'non-response' of PAA compared to PMAA cited, its only-slight alteration to solution viscosity and inability to solubilise hydrophobic dyes as evidence it had no conformational response. However, more recent studies with more sensitive techniques have shown that this is not the case and PAA does indeed go through a lesser swelling-contraction event. As such, it is proposed that the PAA can exist in three potential conformations in the presence of a polymeric bonding partner (**Figure 6**).

We suggest that compacted PAA has no entropic or enthalpic reason to uncoil or swell prior to complexation. Given the combined evidence from two separate sources that (1) most PAM chains are not binding to partners and (2) PAA chains do not swell further apart on PAM binding (in fact there is some evidence of contraction), it seems reasonable to propose that the PAA-PAM complex is not amorphous in nature, and certainly not an extended ribbon/ladder structure.

5. Conclusion

This chapter reviews some of the recent developments in polyacrylate properties and interactions, and delves deeply into their industrial applications to provide both further context and understanding. During the early study many assumptions were made due to the difficulty to analyse these large macromolecules, particularly in dilute solutions, and our understanding of these systems has slowly evolved as more advanced technology with greater sensitivity has facilitated deeper interrogation of these systems [117]. This chapter only touches on a few choice themes of polymer-responsiveness and ignored many of the more challenging aspects of the field. The state of ionisation of all of these polymers has clearly been shown to have an effect on their solution properties, and although the field is still under development after several decades of work, common themes can be seen across the subject dictating macromolecular conformational changes.

Acknowledgements

This book chapter is both an update, summation of, and substantial revision to my Ph.D., work area carried out at the University of Sheffield, originally under Dr. Linda Swanson, who has published extensively on the photophysical analytical techniques described in this paper. For further reference on the application of those techniques in these systems, particularly in the study of polyelectrolytes, please see her book chapter 'Optical Properties of Polyelectrolytes' [26].

Conflict of interest

There are no conflicts of interest to declare.

Thanks

Written following the arrival of, and dedicated to, Jonathan Swift, born in 2017.

Abbreviations

IPC	interpolymer complex formation
DNA	deoxyribonucleic acid
DOM	dissolved organic matter
PAA	poly(acrylic acid)
PAM	poly(acrylamide)
PMAA	poly(methacrylic acid)
PNIPAM	poly(*N*-isopropylacrylamide)

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