



Aggregation behaviour of hydrophobically modified polyacrylate – Variation of alkyl chain length



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ABSTRACT

The aggregation behaviour in aqueous solution of hydrophobically modified polyacrylates, synthesized by Atomic Transfer Radical Copolymerisation (ATRP) of mixtures of alkyl acrylate and t-butyl acrylate and subsequent hydrolysis of the t-butyl acrylate, was investigated by a combination of static and dynamic light scattering with small-angle neutron scattering (SANS). The degree of amphiphilicity was varied by the percentage of alkyl chains and the length of the alkyl chain (butyl to dodecyl), and, in addition, depends strongly on pH via the ionization of the polyacrylate backbone. SANS shows the formation of hydrophobic domains whose size scales with the length of the alkyl chain. The tendency for domain formation increases with the length of the alkyl chains and is much more pronounced for lower pH, while at high pH the electrostatic charging suppresses the formation of hydrophobic domains for chains shorter than octyl. Then only relatively large and loosely connected aggregates are formed. These hydrophobically modified copolymers show a pronouncedly pH dependent aggregation behaviour that is controlled by the length and percentage of hydrophobic modification and this widely tuneable aggregation behaviour could be interesting for the transport and controlled release of hydrophobic cargo molecules.

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1. Introduction

Hydrophobically modified polyelectrolytes are an interesting class of water-soluble polymers, that in principle combine the properties of polyelectrolytes with the ability to self-assemble spontaneously, due to the hydrophobic interactions that arise from this modification [1–6]. Such systems have also been described thoroughly by theory [7] which has predicted the formation of necklace structures, of hairy, crew-cut, or braided micelles or the self-assembly into wormlike cylindrical micelles, depending on the ratio of block sizes and the ratio of the surface energies of the blocks. For instance, water soluble polymers with hydrophobic modifications will have a tendency to form segregated hydrophobic domains. Often the cross-linking of such domains, through polymer chains that have hydrophobic stickers in different

domains, leads to a substantially enhanced viscosity [8–11], i. e. they are rheological modifiers. A simple and classical case of hydrophobic cross-linking has been achieved for the case of doubly end-capped polymers where interconnected networks are frequently formed either by pure self-assembly or by connecting microemulsion droplets [12–15] with the corresponding ability to rheological modification, as it is frequently employed in commercial applications. More recent work then has also shown that the number of hydrophobic end-caps per polymer is a viable tool for controlling the rheological properties of amphiphilic networks formed by the polymers themselves [16] or when they cross-link microemulsion droplets [17,18]. It might be noted that one may also have polyelectrolyte gels with a hydrophobic modification, where microphase separation will be observed and such gels may show pH-dependent swelling [19,20].

pH-sensitive polymeric systems have been studied widely for the case of block copolymers with one or many polyelectrolyte blocks [21,22]. For weakly hydrophobic copolymers it has for

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instance been observed that for the case of P(nBA-stat-AA)-b-PAA di- and triblock copolymers (nBA: n-butyl acrylate, AA: acrylic acid) one can switch from having micelles to complete disintegration of the aggregates by raising the degree of ionisation [23]. For more hydrophobic block copolymers, such as ones made of poly(isobutylene)-block-poly(methacrylic acid) (PIB-b-PMAA) it has been observed that the formed micelles become smaller with increasing degree of ionisation, in agreements with simple packing parameter arguments [24]. And even for their interpolyelectrolyte complexes a reversible pH response has been confirmed [25]. A similar tendency for substantially reduced tendency for aggregation had been reported before for micelles of poly(styrene)-block-Poly((sulfamatercarboxylate) isoprene) copolymer micelles [26], i. e. even for systems where the hydrophobic block is below its glass transition point. Furthermore such pH dependent assembly of block copolymers is not only restricted to the formation of micelles but it has also been reported that vesicle formation can be switched on by raising the pH for poly[2-(methacryloyloxy)ethyl phosphoryl choline]-block-2-(diisopropylamino)ethyl methacrylate copolymers [27]. Of course, such pH response of copolymer micelles is also a very important aspect in designing drug delivery systems [28], a topic that will not dwell on in more detail here.

Of course, end-capped water-soluble polymers and block copolymers with polyelectrolyte chains are just a limiting case of hydrophobic modification and electrostatic stabilization. For copolymers one has easily the option for a fully continuous variation of the extent of hydrophobisation along the backbone of an otherwise hydrophilic polymer. For instance for statistical copolymers, one can tune the amphiphilicity of this polymeric system by the content of a hydrophobic monomer mixed with a hydrophilic monomer. Particularly interesting in that context is using a polyelectrolyte as water-soluble polymer with a multiple number of hydrophobic stickers, where the extent of charging can be controlled by pH, which is the case for polycarboxylates such as polyacrylate or polymethacrylate in a convenient pH-range. A hydrophobic modification may easily be introduced by having alkyl acrylate esters in the copolymer. The hydrophobicity is then controlled by the length of the alkyl chain of the ester and the percentage of hydrophobic substitution. In addition, it depends on pH, as at low pH the extent of ionisation of the polyacrylate backbone is low and the formed polyacrylic acid is itself rather hydrophobic and in pure form not even water-soluble. It should be mentioned that such copolymers are also in commercial use, as for instance in the case of Kollicoat MAE, which is a copolymer of methacrylic acid and ethyl acrylate, which is widely used as a film former, for coatings, and for drug delivery [29]. Such compounds are also often referred to as polysoaps and for instance the case of an alternating copolymer of maleic acid and alkyl vinyl ether with variation of the alkyl chain from butyl to hexadecyl has been studied intensely by means of fluorescence measurements. These experiments [30] showed that the extent of microdomain formation depends largely on the length of the alkyl chain and hardly occurs for alkyl chains shorter than octyl.

Similarly hydrophobically modified polyacrylates (PAA), which contained statistically dodecyl or octadecyl modified acryl amide units, have been investigated by means of pyrene fluorescence and ^{13}C NMR. Here association of the alkyl units was only observed above a certain total concentration and the formed aggregates had lower aggregation numbers and higher polydispersity than the corresponding pure ionic micelles [31]. In contrast, the molecular weight of the polymers was found to have rather little effect on the association behaviour. Finally also PAA with perfluoroalkyl side chains have been studied with respect to their associative behaviour, where the perfluorinated chains lead to stronger aggregation than the corresponding hydrocarbon modification and at sufficient

concentration such systems show pronounced viscosity increase [32].

Structurally similar systems of amphiphilic statistical copolymer samples of sodium 2-(acrylamido)-2-methylpropanesulfonate and n-hexyl methacrylate with different degrees of polymerization and compositions have been investigated where it was found that they form aggregates with 2–7 polymer chains and possessing 1–5 hydrophobic microdomains, where the structures formed depend on the degree of polymerization and composition [33]. Such systems were also investigated with respect to their aggregation behaviour in water/methanol solvent mixtures [34]. For the case of statistical copolymers of 2-(acrylamido)-dodecanesulfonic acid (AMC12S), with 2-(acrylamido)-2-methylpropanesulfonic acid (AMPS) the formation of multimolecular aggregates has been observed [35]. Similar copolymers with a hydrophobic dodecyl chain and based on different amino acids were studied by light scattering and fluorescence. These investigations showed that the interchain aggregation increases with content of the hydrophobic modification, while it decreases with the hydrophobicity of the amino acid residue in the copolymer. Here then flower micelles with minimum loop size are formed [36]. It might be noted that also the formation of multi-chain aggregates has been observed for the case of chitosan hydrophobically modified with 4 mol% of n-dodecyl chains [37]. For the case of amphiphilically modified chitosan rather large aggregates with diameters of 100–300 nm have been observed, that shrink substantially with increasing pH as the chitosan backbone then loses its hydrophilicity [38].

Accordingly, so far quite a bit of work has been done on the properties and aggregation behaviour of hydrophobically modified polyelectrolytes. However, systematic studies on the dependence of the aggregation behaviour as a function of the chain length of the hydrophobic modification for well-defined polymers are still largely missing. Therefore in our work we were addressing this issue for the case of rather short copolymers of acrylic acid and alkyl acrylate (degree of polymerization ~ 100), as they can be generated in a statistical fashion and with rather low polydispersity by means of atomic transfer radical copolymerisation (ATRP). In that context it has to be noted that previous work on the kinetics of radical polymerization of hydrophobically modified acrylates has shown that their rate increases with increasing length of the hydrophobic modification [39]. This means that our statistical copolymers should also not have a fully random distribution of the monomer units, but are expected to have a tendency for having the hydrophobic monomer polymerized initially, and this even more so the more hydrophobic the monomer. This then shall result in a copolymer with a gradient of monomeric units along its backbone, but this effect should also not be too pronounced as only an increase of the propagation rate coefficient by 3–4% per CH_2 has been reported [39]. In our work we then explored to what extent such compounds do self-assemble and how the aggregation properties depend on the percentage of hydrophobic modification (controlled by the amount of hydrophobic monomer), the length of the hydrophobic side-chain, and the pH. This is interesting as such systems can be expected to be rather versatile with respect to their aggregation behaviour and should have a largely enhanced tendency for aggregation at low pH, as schematically depicted in Fig. 1. Accordingly we expect tunable self-assembly, as it is of relevance for the solubilisation and release properties. All this is then of prominent relevance for their potential use in cosmetic or pharmaceutical applications, but also in general, for their use as amphiphilic building blocks in more complex systems.

In the following, we will discuss the synthesis and characterisation of such copolymers with a focus on their aggregation behaviour in aqueous solutions as a function of the molecular composition of the copolymers. They were prepared with alkyl side

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