

SYNTHESIS OF HIGHLY BRANCHED AND HYPERBRANCHED SODIUM 2-ACRYLAMIDO-2-METHYLPROPANESULFONATE IN AQUEOUS MEDIA VIA SELF-CONDENSING AGET ATRP

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Polyelectrolytes find numerous applications in colloid chemistry, cosmetic and biomedical industry. Synthesis of such polymers with well-defined and complex architecture using the new techniques of controlled/"living" radical polymerization such as nitroxide-mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible-addition fragmentation chain transfer (RAFT) in aqueous media is therefore of significant importance.¹

In this contribution we report the preparation of highly branched poly(sodium 2-acrylamido-2-methylpropane-sulfonate) (PAMPS) by self-condensing activators generated by electron transfer atom transfer radical polymerization - AGET ATRP - in aqueous media. In order to obtain branched PAMPS, a comonomer 2-(2-bromopropionyloxy) ethyl acrylate (BPEA) was utilized as a branching unit (*inimer*) under AGET ATRP conditions. It was found that the presence of pyridine in the reaction mixture was essential since it facilitated the reaching of homogeneity of the system and behaved as a co-ligand improving stability of Cu-catalyst in aqueous media. Carrying out the reaction in mixtures of water and pyridine (35-50% of the latter), branched polymers containing branching units of 10-30% were obtained. All the samples of branched PAMPS were transparent brittle solids, visually soluble in water and methanol. They were, however, insoluble, in DMF and pyridine.

Dynamic light scattering was used to examine solution dynamics in methanol, deionized water, 0.1 M HCl, 1 M HCl and 0.15 M NaCl aqueous solutions in a dilute concentration regime ($c^* > c \leq 2 \cdot 10^{-2}$ g/mL). In methanol and pure water an extensive coil expansion was observed due to strong charge repulsion within the branched polymer structure. However, the dimensions drastically decreased upon addition of acid or salt and the unimodal correlation functions for all branched polyelectrolytes were observed with the hydrodynamic radii R_h ranging from 9.6 to 13.2 nm. The hydrodynamic sizes remained essentially unchanged with the variation in the acidity of the aqueous solutions which is a typical behavior of strong polyelectrolytes exhibiting a high degree of ionization.

In order to elucidate the effect of branching on solution properties linear PAMPS were also synthesized using AGET ATRP.

[1] Qiu J., Charleux B., Matyjaszewski K. *Prog Polym Sci*, **2001**, 26 (10), 2083-2134.

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