

Thermodynamic behavior of hydrophobically modified polyacrylamide containing random distribution of hydrophobes: Experimental and theoretical investigations

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ARTICLE INFO

Article history:

Received 11 February 2013

Received in revised form

16 March 2013

Accepted 20 March 2013

Available online 3 April 2013

Keywords:

Polyacrylamide

Associating polymer

Self-assembling

ABSTRACT

Two series of Hydrophobically Modified Polyacrylamides (HMPAMs) were prepared by free radical copolymerization of trimethylsilylacrylamide with 3-pentadecylcyclohexylacrylamide (PDCAM) or dodecylacrylamide (DDAM) followed by removal of trimethylsilyl protecting groups. The solution properties of HMPAMs were studied in dilute aqueous solution by fluorescence spectroscopy, NMR and viscometry. The properties in aqueous solution of HMPAMs clearly displayed the formation of hydrophobic interactions between alkyl stickers. While dodecyl containing HMPAMs mainly showed a progressive collapse of the copolymer coil with the increasing fraction of hydrophobic moieties (weak intra-chain associations), pentadecylcyclohexyl groups containing HMPAMs exhibited a much lower solubility in water due to strong intra- and inter-chain associations. Experimental data were analyzed using the mean field theory developed by Semenov and Rubinstein (SR) for associating polymers. Using a set of realistic parameters, taking into account the solubility of the backbone, the fraction of stickers and the strength of hydrophobic attractions, we show that the SR model offers a quantitative description of the thermodynamic properties of HMPAMs in terms of individual and collective behavior of polymers chains; i.e. swelling and phase separation, respectively.

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1. Introduction

Hydrophobically modified water-soluble polymers are hydrophilic macromolecules containing a small fraction of hydrophobic groups or stickers, that are distributed along the polymer chain or present as end groups [1,2]. In aqueous environment, the stickers self-associate so as to minimize their contact with water molecules giving rise to hydrophobic association. The polymer chains may form intra- or inter-molecular interactions depending on their concentration with intra-molecular interactions dominating in the dilute regime and intermolecular associations prevailing above a certain critical concentration, leading to the formation of transient networks [3–8]. The self-assembling behavior is reversible in nature as hydrophobic interactions can be disrupted under high shear stress and reformed with decreasing shear. These polymers, which are also regarded as self-healing assemblies in solution, exhibit unique viscoelastic properties as compared to other high molecular weight water soluble polymers without associating groups. They play a major role as thickeners and viscosity modifiers in a variety

of water-borne technologies including paints, inks, drilling fluids, pharmaceutical and cosmetics. Moreover, these polymers are also of considerable technological interest, since micelle-like microdomains can dissolve and carry hydrophobic molecules in aqueous media [9–11].

Presently, a large variety of associating water-soluble polymers have been developed with a strategy which considers the following: 1) the architecture of the associating polymer, with a random or block distribution of the hydrophobic stickers along the chain or at the end as in the case of telechelic polymers, 2) the nature of the water-soluble backbone which could be neutral, responsive or ionic and 3) the molar fraction and nature or hydrophobicity of the stickers [12–31]. On the basis of these characteristics, a quantitative description of the associating behavior (thermoreversible gelation and tendency for phase separation) has been proposed in the last two decades for a few simple cases assuming either telechelic polymers or linear polymers with many associating groups [32–44]. Among these models, one of the simplest one is a system of polymer chains containing a large number of stickers randomly distributed along the macromolecule, which are able to form pairwise association. This model, initially introduced by Tanaka [32] and reconsidered to some extent by

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Semenov and Rubinstein [37], gave a detailed description of the mean field theory of associative polymers. They have shown that self-assembling and reversible network formation was accompanied by a tendency for phase separation which might occur even under mild solvent conditions. Using the quality of solvent, the molar fraction of stickers and their binding energy as key parameters, Semenov and Rubinstein's theory (SR model) gives a clue to predict the thermodynamic behavior of associating polymer solutions and their dynamic properties. In the framework of this theory, and limiting the discussion to nonionic linear water-soluble polymers containing a large number of stickers per chain, Hydrophobically Modified Polyacrylamides (HMPAMs) are certainly the most representative one under this category. They have been widely studied in recent years since they overcome some of the drawbacks of their unmodified or partially hydrolyzed analogs, which include sensitivity to mechanical degradation, presence of electrolytes and more particularly multivalent cations in the case of ionic polyacrylate derivatives. Therefore, HMPAMs have emerged as promising materials in various fields such as tertiary oil recovery, drilling fluids, hydraulic fracturing and drag reduction [3,45,46].

HMPAMs can be synthesized either by chemical modification of polymers or by copolymerization of hydrophilic and hydrophobic monomers. The chemical modification of polyacrylamide with alkylbromide in homogenous conditions (DMSO) has been reported by several authors like François et al. [47] and Wu et al. [48]. However, it is rather difficult to identify a common solvent for the dissolution of a very hydrophilic backbone and hydrophobic moieties, during the chemical reaction. Similarly, the copolymerization of acrylamide with a hydrophobic comonomer in homogenous medium involves the use of highly polar solvents for polymerization due to the insolubility of acrylamide in non polar organic solvents. This generally results in polymer chains with low molecular weight due to chain transfer reactions as well as polymers with compositional heterogeneity resulting from differences in the reactivity ratios of the monomers [48]. These structural factors dramatically influence the rheological properties of the final polymer solution.

In order to overcome the above problems, the most widely used method for the synthesis of HMPAM's is the micellar technique where an appropriate surfactant is incorporated to solubilize the hydrophobic monomer in aqueous medium [6,49–51]. The distribution of stickers in the resulting polymers can be blocky and the blockiness depends on the amount of surfactant used and the reactivity ratios of the monomers. An extensive work has been done in this regard by Candau and coworkers who have studied in detail the different factors which influence the structure of the resulting HMPAM [49,52–55]. They have also shown that entangled solutions of HMPAM obey the scaling laws of the sticky reptation model proposed by Leibler et al. [33] and their data were also used by Semenov and Rubinstein to highlight the validity of their qualitative predictions about the scaling relations [40]. Similar conclusions have been drawn on random copolymers of hydrophobically modified N,N-dimethylacrylamide [56], but to the best of our knowledge no studies on thermodynamic swelling properties have been reported on free radically synthesized HMPAMs containing random distribution of hydrophobes.

In the present article we report new studies on thermodynamic properties of Hydrophobically Modified Polyacrylamides containing random distribution of hydrophobes. These copolymers were obtained by free radical solution copolymerization of trimethylsilylacrylamide with two different hydrophobic comonomers, namely 3-pentadecylcyclohexylacrylamide [PDCAM] or dodecylacrylamide [DDAM]. The resultant copolymers containing trimethylsilyl protecting groups were finally deblocked to obtain HMPAMs. These Hydrophobically Modified Polyacrylamides self-

assemble in water at low concentration and exhibit very different behavior in dilute solution with regard to the nature and the content of the hydrophobic substituent. Using a set of realistic parameters that take into account the characteristics of the polymer chains, we show that the SR model offers a very good description of the phase behavior of HMPAM, in terms of individual and collective behaviors of polymers chains; i.e. swelling and phase separation, respectively. Moreover, by comparing the theory with experimental data obtained by viscometry, we emphasize that the SR model is not only qualitative but really gives a semi-quantitative description of the self-assembling behavior of the considered HMPAM polymers.

2. Experimental part

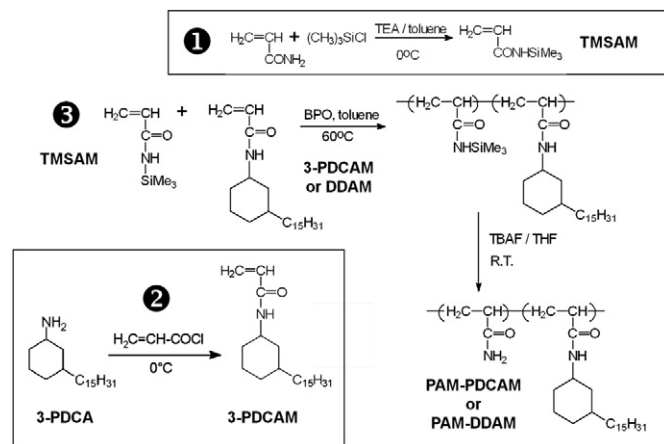
2.1. Materials

3-Pentadecylcyclohexylacrylamide and dodecylacrylamide were prepared in our laboratory. Acrylamide, acryloyl chloride (Aldrich), dodecylamine (SISCO), tetrabutyl ammonium fluoride (1 M solution in THF) (Aldrich), acetone, isopropanol (Merck), trimethylsilyl chloride (Spectrochem), dichloromethane, anhydrous sodium sulfate, potassium hydroxide, sodium hydrogen carbonate and benzoyl peroxide (S.D. Fine Chem) were used as received. Water was purified with a MILLIPORE system combining inverse osmosis membrane (Milli RO) and ion exchange resins (Milli Q).

2.2. Synthesis of HMPAMs

Two series of Hydrophobically Modified Polyacrylamides (HMPAMs) were prepared in homogenous conditions by free radical copolymerization in solution of trimethylsilylacrylamide with 3-pentadecylcyclohexylacrylamide (PDCAM) or dodecylacrylamide (DDAM) followed by removal of trimethylsilyl protecting groups. The synthesis follows a 3-step procedure that is summarized in Scheme 1.

In the first step, a hydrophobic trimethylsilylacrylamide (TMSAm) was prepared in dry toluene by reaction of acrylamide with a small excess of chlorotrimethyl silane in the presence of triethylamine. In step 2, dodecylacrylamide (DDAm) and 3-pentadecylcyclohexylacrylamide (PDCAM) were prepared by reaction of acryloyl chloride with amino derivatives, dodecylamine and 3-pentadecylcyclohexyl-amine (3-PDCA) respectively in dry chloroform. The synthesis of 3-PDCA from cashew nut shell liquid was



Scheme 1. Synthesis of ① trimethylsilylacrylamide (TMSAm), ② hydrophobic comonomers (dodecylacrylamide (DDAM) and 3-pentadecylcyclohexylacrylamide (PDCAM)) and ③ acrylamide copolymers.

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