

SOLID-STATE PHYSICS

OPTIMAL SIZE OF HYDROPHOBIC ASSOCIATES IN AQUEOUS SOLUTIONS OF HYDROPHOBICALLY MODIFIED POLYACRYLAMIDE

Yu. A. Shashkina, V. A. Smirnov, and O. E. Filippova

E-mail: shashkina@polly.phys.msu.ru

Hydrophobic association of hydrophobically modified polyacrylamide in aqueous solutions was studied by fluorescence spectroscopy using pyrene as a probe. It is shown that an increase in the amount of associating *n*-nonylacrylamide units in a polymer leads to the increase in the amount of hydrophobic associates, with the average size of one associate remaining unchanged. Similar regularities are observed in a salt medium as well (in the presence of sodium chloride), however, in this case the average size of associates is much larger.

INTRODUCTION

Associating polymers attract much attention due to their ability of molecular self-organization. They contain hydrophilic units responsible for water solubility of a polymer and hydrophobic units that are responsible for association. Formation of intermolecular associates increases solution viscosity and finally leads to formation of physical gel in which the associates act as cross-links between polymer chains [1–6]. Due to this property associating polymers are extensively used as thickeners in cosmetics, medicine, food industry, manufacture of aqueous paints, and oil production [7–10]. One of the promising associating polymers is hydrophobically modified polyacrylamide (HMPAA). It is used in oil production to prevent water ingress into a well [9, 10].

The associating properties of HM polyelectrolytes can be controlled within broad limits by varying the amount of hydrophobic associating units that promote association and charged hydrophilic units that counteract association. The influence of these factors on rheological properties of HMPAA solutions was thoroughly studied in [1, 2, 7], however, hydrophobic association at a molecular level has not been adequately studied, i. e., the percentage of hydrophobic groups included in associates, concentration of associates and their aggregation number (the number of hydrophobic groups in an associate) have not been determined. This information is important because it is these associates that are responsible for the increase of the viscosity of associating polymer solutions.

The objective of this study was to characterize at a molecular level hydrophobic association of HMPAA with different amounts of hydrophobic units in water media. Apart from acrylamide units, the polymer under study contained 10 mol.% of charged units of sodium 2-acrylamido-2-methyl-1-propanesulfonate and 0.5–1.5 mol.% of hydrophobic *n*-nonylacrylamide units. Hydrophobic association was studied by two methods—solubilization of model hydrophobic substance and self-extinction of a fluorescence probe.

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EXPERIMENTAL

Sodium chloride was used without previous purification. Pyrene (Fluka Co., purity > 97%) was additionally purified by double recrystallization from ethanol to water. Ethanol (Fluka Co.) was distilled to remove fractions with the boiling point 77.5–77.8 °C. Deionized water was produced by treating distilled water in a Milli-Q unit (Millipore Waters Co.).

The HMPAA samples of chemical structure illustrated in Fig. 1 were synthesized through micellar radical copolymerization of acrylamide, n-nonylacrylamide (0.5–1.5 mol.%) and sodium 2-acrylamido-2-methyl-1-propanesulfonate (10 mol.%) using procedures described in [11]. The molecular weight of the polymers produced was determined by thin-layer gel chromatography in a mixed solvent containing 70 vol.% of 0.1 M NaNO₃ solution in water and 30 vol.% of acetonitrile using sulfonated polystyrene as a standard. The molecular weight of HMPAA was about 2 × 10⁶ g/mol.

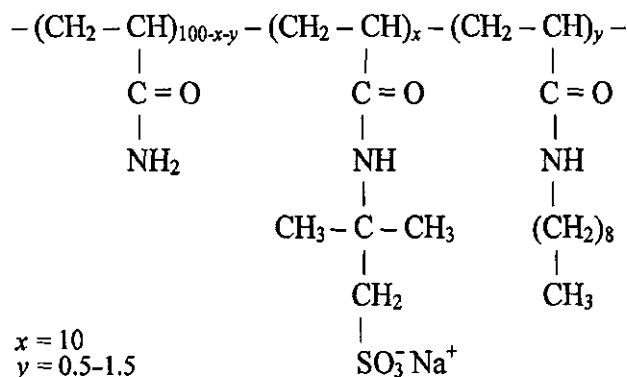


Fig. 1

Chemical structure of the an HMPAA polymer.

Concentration of overlap of polymeric clumps in the HMPAA produced was found by the formula $C^* \cong 1/[\eta]$, where $[\eta] = 9.33 \times 10^{-3} M^{0.75}$ [12]. C^* is shown to be 0.2 wt.%.

Samples for spectral measurements were prepared as follows. A portion of dry polymer was weighed on a balance and deionized water was added to obtain the 2 wt.% polymer concentration in water. Then the aqueous polymer solution was stirred in a magnetic agitator for 3 days. After 3 days when the solution became homogeneous, it was used to prepare a series of 1-ml solutions. A pyrene-in-ethanol solution of concentration in the range 8×10^{-4} – 4.8×10^{-3} mol/l was then added to each of the 1-ml solutions. So, in each series the polymer concentration was constant, but the pyrene concentration varied. Then the samples were kept at room temperature for 3 days before the measurements started. A similar procedure was used to prepare aqueous polymer solutions in the presence of NaCl.

The pyrene concentration in associating polymer solutions was determined on a spectrophotometer by absorption at a wavelength 338 nm. Absorption spectra were measured in a Hewlett-Packard 8452 A spectrophotometer in 1-cm-thick quartz cells.

The concentration of hydrophobic associates in associating polymer solutions was determined by the method of fluorescence probe self-extinction using the procedures described in [5, 11]. The relationship $\ln([\text{Py}_1]/[\text{Py}]) = -[\text{Py}]/[\text{C}]$ was used to calculate concentration [C] of hydrophobic associates. The total concentration of pyrene [Py] was determined from the pyrene absorption spectrum. The total concentration of associates containing one pyrene molecule, $[\text{Py}_1]$, was found from the pyrene fluorescence spectrum.

Pyrene fluorescence spectra were measured in a Hitachi MPF-4 spectrofluorimeter at an excitation wavelength of 338 nm. The bandwidth of the spectrofluorimeter was 4 nm.

RESULTS AND DISCUSSION

Salt-Free Solutions

A hydrophobic pyrene probe is known to have low water solubility (7×10^{-7} mol/l) [13]. However, if hydrophobic associates are present in water, solubility of pyrene is much higher due to solubilization of hydrophobic pyrene molecules inside the associates. The larger the volume of hydrophobic associates in a system, the higher the pyrene solubility.

Figure 2 presents relationships of the optical density of a 338-nm absorption band versus concentration $[C_{Py}]$ of added pyrene in aqueous polymer solutions containing 0.5 mol.% (curve 1), 1 mol.% (curve 2), and 1.5 mol.% (curve 3) of n-nonylacrylamide hydrophobic units. It can be seen that at low pyrene concentrations optical density at a wavelength of 338 nm grows in direct proportion to the concentration of pyrene. Then, at a certain concentration of pyrene, the optical density reaches its limit and stops varying which indicates saturation of the associating polymer solution with pyrene, i. e., the polymer solution is no more able to solubilize added pyrene. The pyrene concentration at which saturation occurs characterizes the maximal solubility of pyrene in the system.

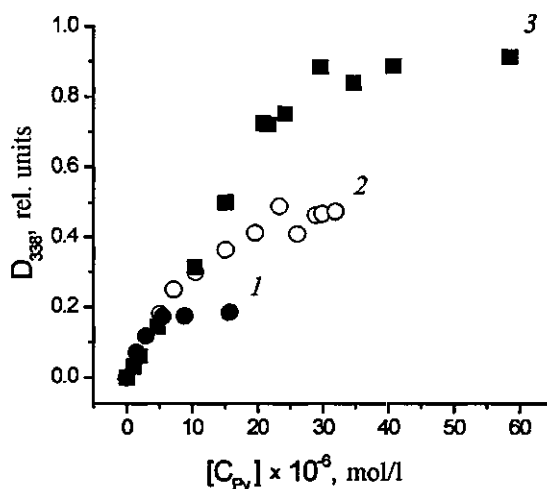


Fig. 2

Optical density of a 338-nm absorption band as a function of added pyrene concentration for polymer solutions containing 0.5 mol.% (1), 1 mol.% (2), and 1.5 mol.% (3) of n-nonylacrylamide hydrophobic units (solvent—water, polymer concentration 2 wt.%).

It is obvious from Fig. 2 that the maximal solubility of pyrene grows with an increase of the percentage of hydrophobic units in a polymer chain. We used the maximal pyrene solubility obtained to calculate the percentage of hydrophobic groups in associates by the method described in [11]. The respective data are listed in Table 1. It can be seen that the percentage of hydrophobic units in associates becomes the higher, the greater the percentage of these groups in the polymer chain, which is explained by a higher concentration of associating groups. Table 1 shows that not all hydrophobic units are incorporated into associates. The result we obtained agrees with the data of [14] for hydrophobically modified sodium polyacrylate in water. The authors relate this to steric hindrances presented by the main polymer chain. It can also be assumed that incomplete incorporation of hydrophobic groups into associates is due to electrostatic repulsion between like-charge units of the polymer.

The method of self-extinction of a hydrophobic fluorescence probe [5] was used to determine concentration of hydrophobic associates in a system. The respective data are presented in Table 1. One can see that the higher the amount of hydrophobic units in the polymer chain, the higher the concentration of associates. Knowing the concentration of hydrophobic associates and their total volume (it is found from the data on maximal pyrene solubility) [11], we calculated the aggregation number, i. e., the average amount

Table 1
Basic Characteristics of Hydrophobic Association of HM PAA with Different Amounts
of Hydrophobic Groups. Polymer Concentration 2 wt.%

Hydrophobic groups amount in polymer, mol.%	Maximal pyrene solubility in system, 10^{-6} mol/l	Concentration of associates, 10^{-6} mol/l	Hydrophobic units amount in associates, %	Aggregation number
Water				
0.5	4.4	6.5	33	59
1	11.7	16.4	48	62
1.5	26.8	40	70	58
0.5-% NaCl solution in water				
1	17.5	15.4	69	99
1.5	26.8	24	70	97

of hydrophobic groups in one associate, by the method described in [11]. The respective data are presented in Table 1. It is seen that the aggregation number is 60 regardless of the percentage of hydrophobic groups in the polymer. A close aggregation number of 50 was observed in aqueous solutions of hydrophobically modified sodium polyacrylate that contained 5 mol.% of hydrophobic n-dodecylacrylate units [15].

The phenomenon of the constant aggregation number of hydrophobic associates was earlier observed in [11] for uncharged HMPAA containing 0.5 mol.% of n-nonylacrylamide hydrophobic units in studies of the effect of polymer concentration in a solution. However, the aggregation number for uncharged HMPAA [11] was much higher (90) than that for charged HMPAA obtained in this work (60). What is the reason for this difference in the size of hydrophobic associates in charged and uncharged HMPAA? It might be assumed that the aggregation number depends on a balance between two counteracting factors. On the one hand, hydrophobic associates grow in size in order to decrease a contact of the hydrophobic groups in the polymer with water. On the other hand, the growth of hydrophobic associates is prevented by steric limitations imposed by polymer chains around an associate and electrostatic repulsion of like-charge polymer units at the surface of an associate. The latter contribution (i. e., electrostatic repulsion) is absent in an uncharged polymer; therefore, the size of associates there is greater. It can be expected that a similar effect of the increase of the aggregation number of hydrophobic associates can also be obtained in a charged polymer by adding a low-molecular salt that screens electrostatic repulsion of like-charge polymer units.

Salt Solutions

Table 1 shows the results of the study of hydrophobic association of polymers in the presence of low-molecular salt NaCl. It can be seen that, similar to salt-free solution, the aggregation number of hydrophobic associates is constant and independent of the amount of hydrophobic n-nonylacrylamide units in the polymer. Nevertheless, in the presence of a low-molecular salt the average size of hydrophobic associates is much larger than their size in salt-free solution (the aggregation number is about 100).

Thus, addition of salt results in a growth of hydrophobic associates which is associated with screening of electrostatic repulsion between like-charge units and also with enhancement of hydrophobic interactions in a salt medium.

It is interesting to note that in salt solutions the percentage of hydrophobic groups incorporated into associates is constant (about 70%) and does not depend on the percentage of hydrophobic associating units in the polymer (see Table 1). A similar result was obtained in [14] for another charged HM electrolyte—HM sodium polyacrylate containing 7 mol.% of hydrophobic n-dodecylacrylate units. In [14] it was shown that addition of 1 wt.% of NaCl to the polymer solution caused an increase in the percentage of hydrophobic groups incorporated into associates. With a further increase of salt concentration, the amount of hydrophobic groups in associates becomes constant (65–70%). The fact that not all hydrophobic side alkyl groups

are included into associates is interpreted by the authors as the effect of steric hindrances presented by the main polymer chain [14].

So, the studies of aqueous HMPAA solutions demonstrated that an increase of the amount of hydrophobic groups in the polymer is not accompanied with a change in the aggregation number of hydrophobic associates. The results we obtained suggest that the associates formed in solutions have the optimal size determined by a balance between hydrophobic association that causes associates to grow and electrostatic repulsion of like-charged polymer units and steric obstacles set by polymeric chains that limit the growth of hydrophobic associates.

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Department of Polymer and Crystal Physics