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Hydrophobic aggregation in aqueous solutions of hydrophobically modified polyacrylamide in the vicinity of overlap concentration

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Abstract

The rheological behavior and hydrophobic association of hydrophobically modified polyacrylamide with 0.5 mol% of hydrophobic n-nonylacrylamide units were studied in the vicinity of the overlap concentration. It was shown that the rheological properties of aqueous polymer solutions are determined by the formation of hydrophobic domains playing a role of physical cross-links between polymer chains. It was observed that a pronounced increase of the viscosity above the overlap concentration is accompanied by the increase of the concentration of hydrophobic domains, but the average size of one domain remains constant.

Keywords: Hydrophobically associating polymers; Fluorescence spectroscopy; Hydrophobically modified polyacrylamide

1. Introduction

Hydrophobically modified (HM) water-soluble associating polymers consist of hydrophilic and hydrophobic units, the latter may be either in side chains or at the ends of macromolecules. In aqueous media the hydrophobic units associate with each other forming hydrophobic domains. If the domains consist of hydrophobic groups of different polymer chains, they play a role of intermolecular cross-links, which can lead to a significant increase of viscosity and finally to the formation of physical gel [1–8]. The ability of hydrophobically associating polymers to enhance viscosity of aqueous solutions is extensively exploited in a variety of practical applications [9], for instance, for blocking water in enhanced oil recovery. For the application in enhanced oil recovery of particular interest are associating polymers based on HM polyacrylamide (PAAm).

To be able to control the rheological properties of such industrially important polymers, it is necessary to understand the aggregation of associating groups at a molecular level. From the classical theory of elasticity it is known that the efficiency of the cross-linking depends on the concentration and functionality of the intermolecular cross-links [10]. Applied to the aqueous solutions of HM associating polymers this concept means that the increase of both the concentration of hydrophobic domains and the average number of polymer chains linked together by one domain can be responsible for the enhancement of viscosity with polymer concentration. The aim of this work is to estimate, which of these factors (concentration or size of domains) determines the observed increase of viscosity of aqueous solutions of HM PAAm. For this purpose the concentration and the size of hydrophobic domains were determined for different polymer concentrations using a fluorescence spectroscopy with pyrene as a probe.

2. Experimental section

Materials. Acrylamide, ammonium persulfate and SDS from Aldrich were used as received. Pyrene was used as fluorescent probe. Pyrene obtained from Fluka was recrystallized three times from absolute ethanol. Water was distilled and deionized.

Synthesis. HM PAAm was synthesized by free-radical micellar copolymerization of acrylamide and *n*-nonylacrylamide. The molar fraction of n-nonylacrylamide in the monomer feed was 0.5 mol%. The synthesis was performed

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in aqueous 4 wt.% solution of SDS at total concentration of comonomers of 3 wt.%. Ammonium persulfate was used as initiator at concentration of 4.4×10^{-3} mol/l. The polymerization was allowed to proceed for 6 h at 50 °C under argon. After that the polymer was twice precipitated in methanol/acetone mixture.

It is known that in the micellar copolymerization of acrylamide with monosubstituted *n*-alkylacrylamide the presence of micelles increases the initial rate of hydrophobic monomer incorporation, which leads to the preparation of copolymers quite heterogeneous in composition [11,12]. The compositional heterogeneity can be significantly reduced, when the average amount of hydrophobic monomer molecules per one SDS micelle is low [12]. Taking this into account, in the present work we used the ratio of hydrophobic monomer molecules per one SDS micelle equal to ca.1.

The molecular weight of the prepared polymer was determined by GPC in 0.1 M $NaNO_3$ in water/acetonitrile (7/3 v/v) mixtures. It was found to be equal to 6×10^5. The details of GPC technique of the determination of molecular weight of HM PAAm are described in details in paper [13]. The value of C^* concentration for aqueous solutions of this polymer was estimated to be ca. 0.5 wt.%. The estimation was made as $C^* \approx 1/[\eta]$ with $[\eta] = 9.33 \times 10^{-3}\ M^{0.75}$ ($[\eta]$ is in g/cm^3) according to Ref. [5].

Samples preparation. To prepare aqueous solutions with different concentrations of polymer the deionized water was added to the polymer. Solutions were stirred at room temperature for at least three days.

Solutions for absorbance and fluorescence measurements were prepared by first pipetting small aliquot (not more than 3 μl) of pyrene stock solutions in ethanol into the flask. Then 1 ml of polymer solution of a given concentration was added to the flask and stirred in the dark for 3 days before the absorbance or fluorescence measurements were made.

Viscosity. Viscosity measurements were carried out on Haake Rheostress RS 150L. The flow curves were in most cases measured using system of coaxial cylinders with double gap of 0.3 mm and mean radius of 20 mm. The obtained viscosity values η were plotted versus the shear stress. Viscosity η_0 was obtained by extrapolation of this dependence to zero shear stress. All measurements were carried out at 20 °C.

Concentration of hydrophobic domains. Concentration of hydrophobic domains was determined using technique elaborated by Flynn and Goodwin [5]. In this technique the concentration of the hydrophobic domains is derived from self-quenching of pyrene molecules absorbed in the hydrophobic cores of the domains. The fluorescence spectroscopy measurements were performed with Hitachi MPF-3 spectrofluorimeter using 5 and 1.5 nm bandpass settings for excitation and emission, respectively. The excitation wavelength was 338 nm.

Limiting solubility of pyrene. To determine the limiting solubility of pyrene in aqueous solutions of HM PAAm different amounts of pyrene probe were added to polymer solution as described above. The total average concentration of added pyrene was varied from 1 to 10×10^{-6} mol/l. After 3 days of equilibration the absorption spectra of pyrene were measured with Hewlett–Packard 8452A spectrophotometer. For analysis of the data an absorbance at 336 nm with respect to the baseline was used. At pyrene concentrations below the limiting solubility $[Py]^s$ the optical density at 336 nm is linearly proportional of the concentration of the added pyrene. As soon as a saturation of polymer solution by pyrene is achieved the measured optical density levels off. Thus, the concentration of pyrene at which the optical density at 336 nm stops to increase with the addition of pyrene was considered as a limiting solubility of pyrene in polymer solution.

3. Results and discussion

Fig. 1 shows that the increase of the concentration of HM PAAm in aqueous solution above the overlap concentration is accompanied by a rather sharp increase of viscosity. Such behavior is typical for many associating polymers [1–8]. We can suggest two main factors, which can contribute to the observed enhancement of viscosity: (i) the increase of concentration of hydrophobic domains and (ii) the increase of the average number of polymer chains linked by one domain. The impacts of these two factors to the change of solution viscosity with polymer concentration are qualitatively estimated in the present contribution.

The concentration of hydrophobic domains C_{agg} was determined using fluorescent technique of self-quenching of pyrene hydrophobic probe [5]. It was shown that the concentration of hydrophobic domains C_{agg} increases with polymer concentration (Fig.2). From the comparison of Figs.1 and 2 it is evident that a sharp rise of viscosity takes place simultaneously with the increase of concentration of hydrophobic domains.

Now let us estimate the average aggregation number N_{agg} of hydrophobic domains. Usually, the average aggregation

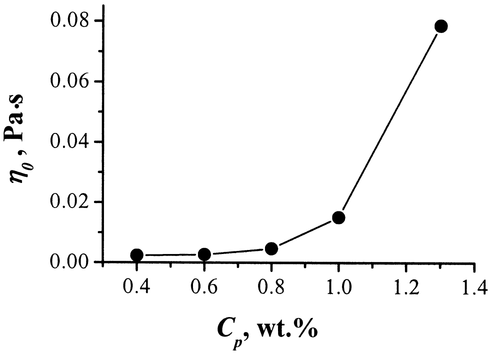

Fig. 1. The dependence of the viscosity η_0 at zero shear stress on polymer concentration for aqueous solutions of HM PAAm C_p.

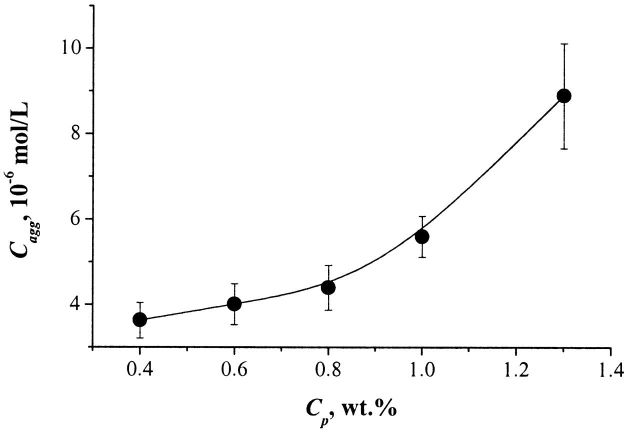

Fig. 2. The dependence of the concentration of hydrophobic domains C_{agg} on the concentration of HM PAAm C_p.

number N_{agg} is expressed by following simple relation [14–16]

$$N_{agg} = C_{C9}/C_{agg}, \tag{1}$$

where C_{C9} is a concentration of hydrophobic alkyl side groups of the polymer in solution. This expression is exact, however, only in the case, when all hydrophobic groups of the polymer are included in the hydrophobic domains. Meanwhile, in the number of experimental studies of aqueous solutions of hydrophobically associating polymers [17,18] it was shown that a fraction of the aggregated hydrophobic groups among all associative groups of the polymer can be far below unity. Thus, the real number of the hydrophobic groups participating in the formation of the domains should be taken into account to avoid an overestimation of the average aggregation number N_{agg}.

The fraction of aggregated alkyl side groups of associating water-soluble polymers can be determined by NMR. The corresponding technique was elaborated by Iliopoulos and Petit-Agnely [17]. This technique exploited the fact that the chemical shifts of the atoms of the free and aggregated terminal methyl groups differ significantly. Thus, the integration of the components of the splitted signal of the atoms of these methyl groups allowed one to calculate the fraction of free and aggregated side chains.

In our case the application of NMR measurements is rather problematic because of too low concentration of the associating groups in the polymer. Therefore, the alternative experimental procedure was used to estimate the fraction of hydrophobic groups included in the domains. This procedure was first described in Ref. [19] and is based on measurements of the limiting solubility of the pyrene probe $[Py]^s$ (Fig.3). Following earlier numerous studies [14–16, 20–26] it was assumed that pyrene molecules are preferentially solvated in hydrophobic cores of domains formed in aqueous solutions of HM PAAm and the concentration of pyrene molecules solubilized in these domains $[Py]^s_{agg}$ at saturation is directly proportional to the volume fraction of the domains ϕ_{agg} [15,16,21,22,24,27].

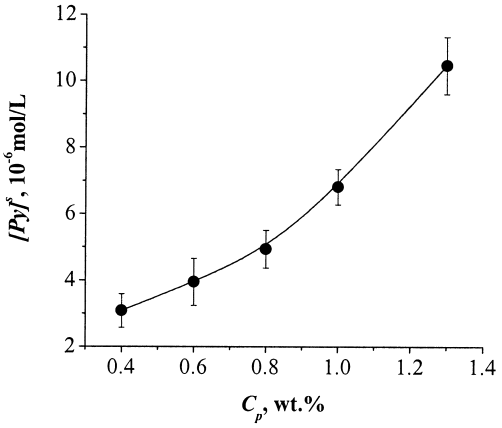

Fig. 3. The dependence of the limiting solubility of pyrene $[Py]^s$ on HM PAAm concentration C_p.

$$[Py]^s_{agg} = [Py]^s - [Py]^s_w = A\cdot\phi_{agg}, \tag{2}$$

where $[Py]^s_w$ is a limiting solubility of pyrene in water, which is approximately equal to 7×10^{-7} mol/l [27], and A is a constant. The investigation of pyrene solubility in aqueous solutions of low molecular weight surfactants (e.g. SDS) showed [26] that the limiting solubility of pyrene molecules inside hydrophobic cores of surfactant micelles is approximately equal to the limiting solubility of pyrene in saturated hydrocarbons having the same number of carbon atoms as in hydrophobic tails of surfactant molecules. In Ref. [19] it was shown that this is valid not only for micelles of low molecular weight surfactants, but also for hydrophobic domains formed in solutions of HM polymers. Taking this into account, it is possible to calculate the concentration of hydrophobic groups of HM PAAm participating in the formation of hydrophobic domains n_{agg}

$$n_{agg} = \frac{\phi_{agg}}{\nu_{C9}} = \frac{[Py]^s_m}{[Py]^s_{C9}\nu_{C9}} \tag{3}$$

where $[Py]^s_m$ is the limiting solubility of pyrene in the solution of HM PAAm, $[Py]^s_{C9}$ is a limiting solubility of pyrene in n-nonane and ν_{C9} is a molar volume of n-nonyl tails of the polymer. For calculations the limiting solubility of pyrene in n-nonane $[Py]^s_{C9}$ and molar volume of n-nonyl tails of the polymer ν_{C9} were taken to be equal to 0.074 mol/l and 0.164 l/mol, respectively. The value of the limiting solubility of pyrene in n-nonane $[Py]^s_{C9}$ was assumed to be the same as the limiting solubility of pyrene in n-decane 0.074 mol/l. The latter value was determined experimentally as described in the experimental part. The same value was obtained in Ref. [26]. The molar volume of n-nonyl tails of the polymer ν_{C9} was calculated according to Ref. [28].

The ratio of the obtained value of concentration of hydrophobic groups included in the aggregates n_{agg} to the total concentration of n-nonyl hydrophobic groups in the system C_{C9} gives the fraction of the aggregated side groups of the polymer F_{agg}. Fig.4 illustrates the dependence of the

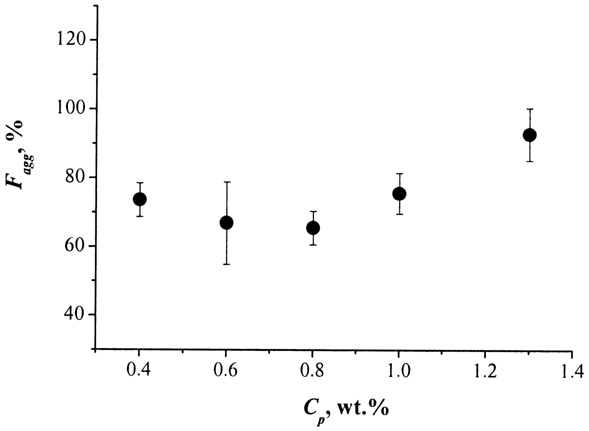

Fig. 4. The effect of concentration of HM PAAm in aqueous solution C_p on the fraction of hydrophobic side groups of the polymer included in the aggregates F_{agg}.

fraction F_{agg} on the polymer concentration. At low polymer concentrations only about 70 mol% of hydrophobic groups are included in the aggregates. With the increase of polymer concentration the fraction of aggregated hydrophobic groups tends to 100 mol%. The observed effect is related to the fact that at the increase of polymer concentration the conformational entropy loss in the process of aggregation becomes smaller, which favors the aggregation and makes almost all hydrophobic groups in the system being included in the aggregates.

Thus, given the concentration of hydrophobic groups included in the domains n_{agg}, the average aggregation number N_{agg} is simply expressed as

$$N_{agg} = n_{agg}/C_{agg}. \tag{4}$$

The obtained dependence of aggregation number N_{agg} on the polymer concentration is presented in Fig.5. From the figure it is seen that the average aggregation number slightly increases with polymer concentration and levels off above 0.8 wt.% of polymer in solution. Thus, the aggregation number remains unchanged in a range of polymer concentrations (0.8–1.3 wt.%), at which a significant increase of viscosity is observed (cf. Figs. 1 and 5). Therefore, a sharp increase of viscosity is due mainly to the increase of the concentration of hydrophobic domains, while the average size of one domain remains almost unchanged.

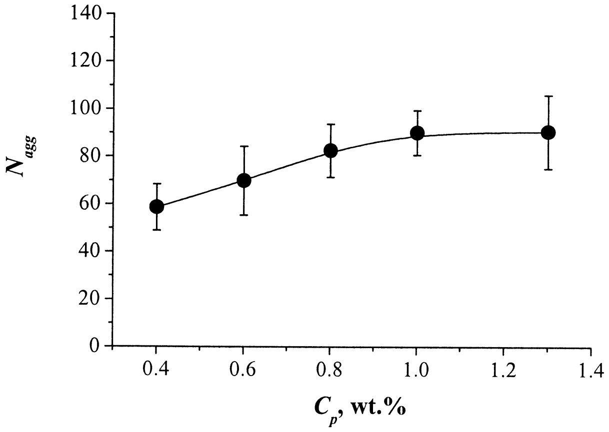

Fig. 5. The dependence of the aggregation numbers of hydrophobic domains N_{agg} on the concentration of HM PAAm C_p.

Table 1
The values of aggregation numbers of micelles formed by some low molecular weight surfactants in aqueous solutions

Surfactant	Aggregation number N_{agg}	Ref
R_9–COO–$(C_2H_4O)_7$–CH_3	86	[30]
R_9–COO–$(C_2H_4O)_{10}$–CH_3	58	[30]
R_{12}–$(CH_3)_2NO$	76	[28]
R_9–SO_4Na	33	[28]
R_9–COONa	38	[30]

The analogous behavior was observed recently for HM ethoxylated urethane polymers with associating groups located at the ends of polymer chains. It was shown that for these polymers the value of aggregation number of hydrophobic domains is constant over a limited range of concentrations that spanned a large increase of viscosity at the transition from flower micelles to well-formed networks [29].

The constant value of aggregation number over a certain range of polymer concentrations indicates the formation of hydrophobic domains of optimum size. In the case of uncharged polymers the optimum size of hydrophobic domains is most probably determined by the size of hydrophobic group and by steric hindrances imposed by polymer chains connected to the domain.

The aggregation numbers of hydrophobic domains in HM PAAm are somewhat higher than those in HM poly(sodium acrylate) ($N_{agg} \sim 40$–50 [18]) (the both polymers have hydrophobic side chains) or in solutions of charged low molecular weight surfactants with the same length of *n*-alkyl tail (Table 1). Most probably, this difference is a manifestation of the repulsive electrostatic interactions between charged acrylate groups in the corona of hydrophobic aggregates, which favor the reduction of size of the domains. At the same time, the observed aggregation numbers in HM PAAm are rather close to the aggregation numbers of uncharged low molecular weight surfactants with the same length of *n*-alkyl tail (Table 1).

Thus, the study on the microscopic level of the hydrophobic aggregation in the aqueous solution of HM PAAm reveals that the sharp increase of viscosity with polymer concentration is accompanied by the increase of the concentration of hydrophobic domains, but the average size of one domain remains unchanged.

References

[1] Jiménez-Regalado E, Selb J, Candau F. Macromolecules 1999;32(25): 8580–8.

[2] Volpert E, Selb J, Candau F. Polymer 1998;39(5):1025–33.

[3] Petit E, Iliopoulos I, Audebert R, Szonyi S. Langmuir 1997;13(16): 4229–33.

[4] Noda T, Hashidzume A, Morishima Y. Langmuir 2001;17(19): 5984–91.

[5] Flynn CE, Goodwin JW. In: Schultz DN, Glass JE, editors. Polymers as Rheology Modifiers. New York: American Chemical Society; 1991. Ch 11.

[6] Kramer MC, Steger JR, Hu Y, McCormik CL. Macromolecules 1996; 29(6):1992–7.

[7] Bromberg L. Macromolecules 1998;31(18):6148–56.

[8] Tsitsilianis C, Iliopoulos I, Ducouret G. Macromolecules 2000;33(8): 2936–43.

[9] Finch CA, editor. Industrial Water-Soluble Polymers. Cambridge, UK: The Royal Society of Chemistry; 1996.

[10] Treloar LRG. The Physics of Rubber Elasticity. Oxford: Clarendon Press; 1975.

[11] Biggs S, Hill A, Selb J, Candau F. J. Phys. Chem. 1992;96(3): 1505–11.

[12] Lacik I, Selb J, Candau F. Polymer 1995;36(16):3197–210.

[13] Blagodatskikh IV, Sutkevich MV, Sitnikova NL, Churochkina NA, Pryakhina TA, Philippova OE, Khokhlov AR. J Chromatogr 2002; 976:155–64.

[14] Sato Y, Hashidzume A, Morishima Y. Macromolecules 2001;34(17): 6121–30.

[15] Noda M, Morishima Y. Macromolecules 1999;32(14):4613–40.

[16] Vorobyova O, Yekta A, Winnik MA, Lau W. Macromolecules 1998; 31(25):8998–9007.

[17] Petit-Agnely F, Iliopoulos I. J. Phys Chem B 1999;103(23):4803–8.

[18] Petit-Agnely F, Iliopoulos I, Zana R. Langmuir 2000;16(25):9921–7.

[19] Philippova OE, Smirnov VA, Shashkina YuA, Ryzhikov BD, Khokhlov AR, Vasiliev VG, Rogovina LZ. Macromol Chem Phys, submitted for publication.

[20] Magny B, Iliopoulos I, Zana R, Audebert R. Langmuir 1994;10: 3180–6.

[21] Araujo Y, Rharbi Y, Huang X, Winnik MA, Bassett DR, Jenkins RD. Langmuir 2000;16(23):8664–71.

[22] Kumacheva E, Rharbi Y, Winnik MA, Guo L, Tam KC, Jenkins RD. Langmuir 1997;13(2):182–6.

[23] Jover A, Nunez ER, Tato JV, Mosquera M. Langmuir 1997;13(2): 161–4.

[24] Almgren M, Wang K, Asakawa T. Langmuir 1997;13(17):4535–44.

[25] Grieser F, Drummond CJ. J Phys Chem 1988;92(20):5580–93.

[26] Almgren M, Grieser F, Thomas JK. J Am Chem Soc 1979;101(2): 279–91.

[27] Yekta A, Duhamel J, Brochard P, Adiwidjaja H, Winnik MA. Macromolecules 1993;26(8):1829–36.

[28] Evans DF, Wennerstrom H. The Colloidal Domain Where Physics, Chemistry, Biology, and Technology Meet. New York: VCH Publishers; 1994. ch. 1,4.

[29] Yekta A, Xu B, Duhamel J, Adiwidjaja H, Winnik MA. Macromolecules 1995;28:956–66.

[30] Shinoda K, Nakagawa T, Tamamushi B, Isemura T, editors. Colloidal Surfactants. Some Physicochemical Properties. New York: Academic Press; 1963.