Effect of Polymer Additive on Inverse Microemulsion Polymerization of Acrylamide

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The effect of polyacrylamide as an additive on preparation of inverse microemulsion toluene—AOT (AOT – sodium bis(2-ethylhexyl)sulfosuccinate)—water—acrylamide—polyacrylamide and on the properties of polymer particles resulting from the free-radical polymerization of acrylamide was studied. It was found that the amount of polyacrylamide which can be added without hindering the formation of the inverse microemulsion depends on the toluene:AOT mole ratio (x_r). Macroviscosity of the inverse microemulsion depends on the value of volume fraction of aqueous phase (water—acrylamide—polyacrylamide), φ_{aw}, in the inverse disperse system. Besides influencing the formation and stability of inverse microemulsion, the presence of polyacrylamide in the inverse micelles enormously increases the final polyacrylamide particle size. On the other hand, addition of polyacrylamide only marginally affects the molecular mass of polyacrylamide formed in polymer particles.

Effect of added polymer on the dispersed particles of the disperse systems was studied in several papers [1—4]. Addition of water-soluble polymers (polymers dissolved in water pools of inverse micelles) and of the polymers partially soluble in water decreases the attractive interactions between water droplets, whereas addition of oil-soluble polymer increases them [4]. The ability of nonionic polymers to associate with the surfactant assemblies was predicted qualitatively on the basis of simple molecular model and illustrative calculations were presented for forecasting the structural transitions in microemulsion systems [5]. Many examples are also known of the incorporation of water-soluble low- and high-molecular mass substances in water pools of inverse micelles in order to carry out chemical reactions on the solute. Thus the use of inverse micelles as microreactors enabled the preparation of tailor-made conjugates of natural and synthetic macromolecules [6].

The possibility of carrying chemical reactions on the macromolecular solute dissolved in water pools of inverse micelles as well as the fact of increasing stability of surfactant assemblies in the presence of water-soluble polymers led us to the idea to polymerize water-soluble monomer in the presence of water-soluble polymer in the water pool of inverse micelle. Such a polymerization system forms during common free-radical polymerization of acrylamide in inverse microemulsion [7] (formation of polyacrylamide due to polymerization of acrylamide). The attempts to add dead polymer in the form of aqueous solution during preparation of inverse microemulsion are usually unsuccessful (formation of a two-phase system and not of a single-phase inverse microemulsion), very probably due to a relatively high concentrations of water-soluble polymer used. Besides this, some problems could be caused also by a molecular mass of the polymer, *i.e.* if the radius of gyration of polymer coil in aqueous solution is much greater in comparison to the size of the inverse micelle [8]. It seems that these problems were not sufficiently explored till now, and new concise data are needed for wider use of micro(nano)reactors in chemical synthesis and preparation of polymer-containing inverse microemulsion.

In this paper the results of the preparation of inverse microemulsions containing besides acrylamide also water-soluble polyacrylamide, and of the subsequent polymerization of acrylamide in these systems, are reported. The aim of this work was to establish quantitative relationships between components of inverse disperse system in order to prepare stable single-phase systems before as well as after polymerization, and to characterize the resulting polymerized disperse systems and the polyacrylamide in polymer particles.

EXPERIMENTAL

Acrylamide (AAm) (puriss., recrystallized; from Serva, Feinbiochimica, GmbH & Co., Heidelberg, Germany), sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (purum; from Fluka Chemie AG, Buchs, Switzerland), toluene (anal. grade; from Lachema, Prague, Czech Republic), and 2-propanol (anal. grade; from Lachema, Brno, Czech Republic) were used without further purification. Dibenzoyl peroxide (DBP) (purum; from Lachema, Prague, Czech Republic) was re-

Table 1. Effect of Polyacrylamide (PAAm) on the Formation and Stability of the Inverse Disperse System[a] at 20 °C

Run	m(AAm) g	m(PAAm) g	Comments
1[b]	–	–	Formation of inverse microemulsion within 5 min after addition and mixing of the oil phase (solution of AOT in toluene) with water.
2[b]	0.4	–	Immediate formation of the inverse microemulsion after mixing oil phase with aqueous solution of acrylamide.
3[b,c]	0.4	≤ 0.02	Inverse microemulsion (m(PAAm)/m(AAm) ≤ 0.05).
4[b]	0.4	> 0.02	Multi-(2- and/or 3-)phase systems.

a) [Toluene]/[AOT] = 20.1; m(water)/m(AOT) = 10.3; $\overline{M}_N$(PAAm) = 6.6×10^4 g mol^{-1}; b) m(toluene):m(AOT):m(water) = 15:3.6:1.5; c) volume fraction, φ_{aw}, of the dispersed phase (water—AAm—PAAm) in inverse microemulsion (φ_{aw} = 8.40 %).

crystallized from ethanol. Distilled water was deprived of oxygen by heating to the boiling point and cooling under stream of nitrogen.

Polymer additive, polyacrylamide, a component for preparation of inverse microemulsion was prepared by polymerization of acrylamide in the mixture of water and 2-propanol (φ_r = 9 : 1) according to the procedure outlined in [9]. Though 2-propanol is a precipitant of polyacrylamide, its minute concentration in aqueous solution did not lead to the precipitation of polyacrylamide formed. The use of 2-propanol, which is an effective chain-transfer agent in acrylamide free-radical polymerization, served for obtaining of polyacrylamide of desired, relatively low molecular mass. Polyacrylamide was precipitated from the water—2-propanol solution by addition of ethanol. Polyacrylamide was then dissolved in distilled water, repeatedly precipitated by addition of ethanol, dried in an oven at 50 °C and stored in a desiccator.

Inverse microemulsion containing acrylamide and polyacrylamide (the latter was applied together with acrylamide as aqueous solution) was prepared by simple mixing of aqueous solution with the toluene solution of AOT and dibenzoyl peroxide. For visual characterization the disperse systems were prepared without dibenzoyl peroxide initiator.

For polymerization of acrylamide in the presence of polyacrylamide the procedure known for polymerization of acrylamide in inverse microemulsion was used [7, 10]. Polymer particle size was measured by a BI Brookhaven Instrument Corporation particle sizer. The diameter of an individual polymer particle obtained at various polymer particle concentrations (on diluting by toluene) was extrapolated to zero polymer particle concentration.

Limiting viscosity number of polyacrylamide precipitated from inverse microemulsion after polymerization (i.e. of the mixture of polyacrylamide added prior to polymerization and of polyacrylamide formed during polymerization of acrylamide) by addition of excess ethanol and following washing with ethanol was determined in water at 25 °C.

Viscosity of the single-phase inverse disperse systems was measured at 20 °C using an Ubbelohde vis-

cometer. Flow times were compared with flow times of liquids of known viscosities (η/(mPa s)).

RESULTS AND DISCUSSION

As can be seen from the data in Table 1, monomer acrylamide favourably affects the formation and stability of inverse microemulsion. Small amounts of added polyacrylamide (up to m(PAAm)/m(AAm) $\leq$ 0.05) do not influence the formation of inverse microemulsion. Addition of PAAm in greater amounts, however, hinders the formation of the inverse microemulsion (Table 1).

In order to obtain a single-phase inverse disperse system characterized by higher ratios m(PAAm)/m(AAm) (e.g. 0.100) it is necessary to increase the concentration of AOT surfactant in the system by choosing a value of the mole ratio [Toluene]/[AOT] = 8.0 (cf. Table 2).

Increase of φ_{aw} values leads to an increase of the macroviscosity of the single-phase disperse system. Contrary to the system toluene—AOT—water—

Table 2. Macroviscosity of the Inverse Microemulsion Prior to Polymerization, η, Polyacrylamide Particle Diameter, d, and Limiting Viscosity Number, [η], of Polyacrylamide Prepared by Polymerization of Acrylamide in the Presence of Polyacrylamide in the Single-Phase Inverse Disperse Systems[a]

Run	φ_{aw}/%[b]	η/(mPa s)[c]	d/nm	$10^{-2} \cdot [\eta]$/(cm^3 g^{-1})
5	16.6	6.1	59	3.80
6	28.6	13.3	87	--
7	37.5	27.5	92	4.47
8	44.4	43.2	–[d]	--
9	50.0	26.7	–[d]	5.40

a) m(PAAm)/m(AAm) = 0.100; m(toluene)/m(AOT) = 8.0; c(DBP) = 1.19×10^{-2} mol dm^{-3} (based on toluene); for $\overline{M}_N$(PAAm) see Table 1; polymerization temperature 60 °C; polymerization time 60 min; b) see Table 1; c) viscosity of the single-phase inverse disperse system prior to polymerization (at 20 °C); d) not reproducible value obtained.

acrylamide [11] only one viscosity maximum (around $\varphi_{aw} = 45\%$) was observed. The viscosity maximum reflects the transition of water-in-oil inverse microemulsion to a bicontinuous microemulsion [11].

Polyacrylamide particle size and limiting viscosity number of polyacrylamide in polymer particles show a tendency to increase with the increasing volume fraction φ_{aw} of the disperse system. This behaviour is similar to that found for inverse disperse systems prepared without polyacrylamide [7, 11, 12].

The dependence of the limiting viscosity number of polyacrylamide in polymer particles and of the polymer particle size on the mass ratio m(AAm—PAAm)/m(water) is shown in Fig. 1.
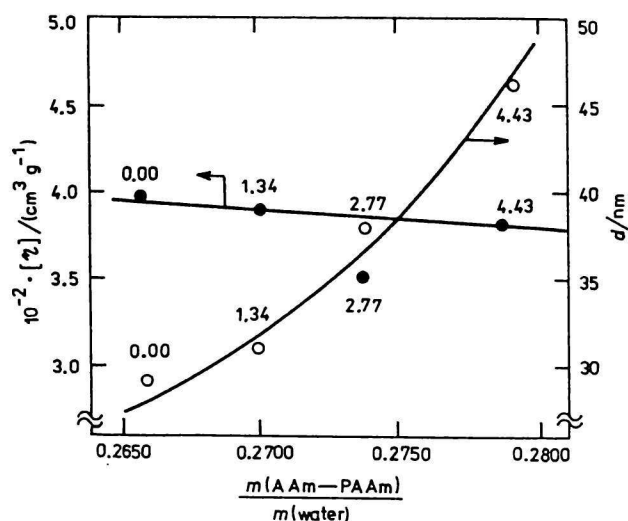

Fig. 1. Dependence of the limiting viscosity number, $[\eta]$, of polyacrylamide in polymer particle and of the polyacrylamide particle diameter, d, on the mass ratio m(AAm—PAAm)/m(water) in the inverse microemulsion system m(toluene):m(AOT):m(water):m(AAm) =15:3.6:1.5:0.4. The value of the mass ratio m(PAAm): m(AAm) as indicated at experimental points. Polymerization temperature: 60 °C. Polymerization time: 60 min. For further details see Tables 1 and 2.

The slight decrease of the limiting viscosity number points at the transfer reactions of growing macroradicals with polyacrylamide. Transfer constant of polyacrylamide radical to polyacrylamide was not reported [13] till now. It can be approximated by the value 6.1×10^{-5} published in [13] for N,N-dimethylacrylamide—poly(N,N-dimethylacrylamide) couple. From the limiting viscosity data presented in Fig. 1 after their transformation into molecular masses [14] of polyacrylamide a rough value $\approx 10^{-5}$ for transfer constant for acrylamide—polyacrylamide couple was calculated by use of Mayo equation [15]. Thus it is clear that the transfer reactions of growing macroradicals with polyacrylamide additive cannot seriously influence the molecular mass of the polymer formed in aqueous phase of the inverse disperse system.

On the other hand, the addition of PAAm significantly increases the polymer particle size. The increase of the ratios m(AAm—PAAm)/m(water) by 0.015 increases the polymer particle size approx. 1.5 times (cf. Fig. 1). For obtaining the same change of polymer particle size in the inverse microemulsion which was prepared without PAAm additive the corresponding increase of the mass ratio m(AAm)/m(water) is by two orders of magnitude greater (1.975) [12].

The effect of added polyacrylamide on the final polymer particle size could be explained by expansion of a part of polyacrylamide chain (e.g. in a form of a loop or a free end) into the interphase [16] formed by AOT surfactant aliphatic carbon chains solvated by toluene. Such expansion increases the number of possible configurations of polymer chain and thus it is entropically favoured.

The insertion of an additive (of low and/or high molecular mass) usually does not significantly affect the inverse micelle size [17]. This problem seems, however, not to be fully clarified because literature brings also contradictory data on the effect of polymer additive on the inverse micelle size (cf. Ref. [4] vs. Ref. [18], for example). Considering the inverse colloidal particle size not to be sensitive to the presence and/or absence of polymeric additive in the water pool of inverse micelle and accepting the expansion of a part of a polymer chain into interphase [16] one should expect that the extent of the collapsed state of polymer chains [8] in polymer particle would be lowered. This is another possible explanation of the added polymer effect on the polymer particle size growth in inverse microemulsion polymerization of acrylamide.

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