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Inverse Microemulsion Polymerization of Oil-Soluble Monomers in the Presence of Hydrophilic Polyacrylamide Nanoparticles

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Summary: A new method for preparation of modified polymer particles in two steps was proposed. Free radical polymerization of an oil soluble vinyl monomer like butyl acrylate in inverse microemulsion containing polyacrylamide particles led to the formation of modified, partly hydrophobized, polyacrylamide particles. For the first step of the process (preparation of polyacrylamide particles in inverse microemulsion) is typical a very high polymerization rate while for the second step (polymerization of an oil soluble monomer (methyl acrylate,ethyl acrylate, butyl acrylate 2-ethylhexyl acrylate, methyl methacrylate, styrene) in the presence of polyacrylamide particles in inverse microemulsion, the reverse is true. The polymerization of an oil soluble monomer in some instances leads to the formation of 2- phase or even 3-phase disperse systems. The polymeric products obtained after precipitation of the polymer particles from the inverse microemulsions by ethanol were extracted by water and/or toluene and analyzed for acrylamide content The separated polymer product contained high content of acrylamide, AAm/oil soluble monomer (butyl acrylate BA, or styrene, S) copolymer (85 % of AAm/BA , ≈ 99 % of AAm/S) besides relatively small amounts of homopolymers of oil soluble monomers (15 % of BA , ≈ 1 % of S homopolymers).

Introduction

Free-radical polymerization in aqueous dispersions in the presence of seed polymer particles is a well known process enabling the preparation of modified polymer particles of various chemical composition and structure [1,2]. Much less attention was paid to the polymerization and copolymerization of vinyl monomers in inverse dispersion systems, e.g. in inverse microemulsions [3] Inverse microemulsions are known to be very sensitive to changes of the compositions and mutual proportions

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of the water- and oil phases [4-8]. The polymerized inverse microemulsions, e.g. polyacrylamide containing inverse microemulsions, are even more sensitive to changes of the compositional and concentrational relations in the disperse system [9]. From the point of colloidal properties of inverse microemulsions (composed from toluene,T, oil soluble monomer, OSM, sodium salt of bis (2-ethylhexyl)sulfosuccinate, AOT, water, W, acrylamide, AAm, sodium dodecyl sulfate, SDS) and intended modification of their hydrophilic polyacrylamide particles it is necessary to prepare the stable inverse microemulsions with the optimal intra phases (e.g. [T]/[AOT], AAm/W, W/SDS) and inter phases (e.g. W]/[AOT], AOT/SDS, OSM/AAm, Φ_{aw}) parameters [3,10]. This assures the obtaining of stable inverse microemulsions with optimal conditions for the realization of the proposed modifications of the polyacrylamide particles of inverse microemulsions. The nature of the vinyl monomer (e.g. the vinyl monomer solubility in water- and/or oil phase) influences the partitioning of the vinyl monomer between oil- and water phase of the inverse microemulsion. The presence of the part of an oil soluble monomer (OSM) in the water phase could influence not only the stability of the inverse microemulsion but also the polymerization and/or copolymerization processes in inverse microemulsion system [8,11-14].

This paper relates to the preparation of tailored hydrophilic polyacrylamide particles and to their modification by an oil soluble vinyl momomer in Winsor IV single-phase inverse microemulsions. Both preparation and characterization of inverse microemulsions prior to and after polymerization as well as kinetics of polymerization of acrylamide and kinetics of polymerization of an oil soluble monomer in the presence of prepared polyacrylamide particles in inverse microemulsion (Two-step process), are reported. Resulted polymeric products in the form of polymer particles in various disperse systems were analyzed for acrylamide content and solubility in water and/or toluene. For comparison some data on the copolymerization of AAm with an oil soluble monomer in inverse microemulsion (One step process) are also presented.

Experimental Part

Chemicals :

Acrylamide (AAm) (puriss., recrystallized; from Serva, Feinbiochimica, GmbH & Co., Heidelberg, Germany), sodium bis (2-ethylhexyl) sulfosuccinate (AOT) (purum; from Fluka Chemie AG, Buchs, Switzerland), sodium dodecyl sulphate (SDS) (purum; from Merck-Schuchardt, Hohenbrunn/München, Germany), toluene (p.a. from Lachema, Prague, Czech Republic) and ammonium peroxodisulfate (APS) (purum; from Lachema, Prague, Czech Republic) were used without further purification. Dibenzoyl peroxide (DBP) (purum; from Lachema, Prague, Czech Republics) was recrystallized from ethanol. Commercially available butyl acrylate (BA) (purum; from Merck-Schuchardt, Hohenbrunn/München, Germany), ethyl acrylate (EA), 2-ethylhexyl acrylate (2-EHA), methyl acrylate (MA), methyl methacrylate (MMA) and styrene (S) all of Sigma-Aldrich (Lambda Life, a.s. Bratislava), were deprived of inhibitor by distillation at reduced pressure of argon. Distilled water used for preparation of inverse microemulsions was deprived of oxygen by heating to the boiling point and cooling under a stream of argon.

Procedures :

Use of polyacrylamide containing inverse microemulsions for preparation of modified polyacrylamide particles by Two-step process.

First step – preparation of polyacrylamide inverse microemulsions.

Acrylamide containing inverse microemulsions were prepared by mixing a solution of AOT in toluene with a water solution of AAm and APS and/or AAm, sodium dodecyl sulphate and APS at room temperature. Inverse microemulsions were then polymerized at 60°C up to nearly 100 % conversion of acrylamide and stored in dark at room temperature before use. For compositions see Table 1.

Second step – modification of polyacrylamide particles of inverse microemulsions by oil soluble monomers.

The polymerisable inverse microemulsions containing the oil soluble monomer and polyacrylamide particles were prepared simply by mixing the polyacrylamide containing inverse microemulsion prepared in the First step with an oil soluble monomer (OSM, like S, MA, EA, BA, 2-EHA, MMA) containing system (inverse microemulsion, solution of OSM, or bulk OSM) in a given mass ratio (for compositions and parameters see Table 1 and Table 2).

Table 1. Compositions (in grams of components per 100 g) of acrylamide and/or oil soluble monomer (OSM) containing systems.

System	T	OSM	AOT	Water	AAm	SDS	APS	DBP	Φ_{aw} [a]
A	73.13	-	17.55	7.31	1.95	-	0.0507	-	0.083
A_1	66.93	-	16.06	13.39	3.57	-	0.0464	-	0.153
A_2	60.46	-	24.18	12.09	3.22	-	0.0419	-	0.141
A_N	72.78	-	17.47	7.28	1.94	0.49	0.0500	-	0.087
B	71.75	2.47	17.81	7.42	-	0.50	0.051	-	0.073
C	-	74.22	17.81	7.42	-	0.50	0.051	-	0.075
C_3	-	74.59	17.90	7.46	-	-	0.052	-	0.070
C_4	-	74.44	17.97	7.44	-	-	-	0.248	0.070
C_1	-	80.43	19.30	-	-	-	-	0.268	0.000
C_{OSM} [b]	-	99.67	-	-	-	-	-	0.332	0.000
C_5 [c]	-	100.00	-	-	-	-	-	-	0.000

[a] Volume fraction of aqueous phase was calculated from the volumes of individual water- and oil- phase components according to the eq.
Φ_{aw} = (Water+AAm+SDS+APS) / [(Water+AAm+SDS+APS)+(T+OSM+AOT+DBP)].

[b] Solution of DBP in OSM (OSM= BA (C_2), MMA (C_6), EA (C_7), MA (C_8), S (C_9), 2-EHA (C_{10})).

[c] BA monomer without additive(s).

The free-radical polymerization of the oil soluble monomer led then to the formation of modified polyacrylamide particles in inverse microemulsions and/or modified polyacrylamide containing disperse systems (see later).

Copolymerization of AAm and oil soluble monomer in inverse microemulsion (one step process).

Here instead of polymerized polyacrylamide inverse microemulsion the non-polymerized acrylamide containing inverse microemulsion was used (Table 1) and mixed with an oil soluble monomer containing system (Table 1) in a given mass ratio (see Table 2). This procedure enables the simultaneous copolymerization of both comonomers in the mixed reaction systems. During initial rapid stage of polymerization polyacrylamide particles are formed [15] and thus these mixed systems gradually become the features of the Two step process (slow polymerization of an oil soluble monomer in the presence of hydrophilic polyacrylamide particles).

Table 2. Composition and parameters of the mixtures of the polymerized (A, A_1, A_2, A_N) inverse microemulsions with nonpolymerized (B, C, C_1, C_2, C_3, C_4, C_5) oil soluble monomer OSM containing systems. Mixtures are formulated on the weight basis. For compositions of individual components of the mixtures see Table 1.

Mixtures	Φ_{aw}	OSM/AAm [a)]	AAm % [b)]	[T]/[AOT] [c)]	[W]/[AOT] [d)]	AAm/W [e)]
A	0.083	0.000	1.95	20.10	10.29	0.266
A + B	0.078	1.272	0.98	19.77	10.29	0.133
A + 0.1C	0.082	3.806	1.77	18.24	10.29	0.242
A + 0.1C_3	0.082	3.825	1.77	18.24	10.29	0.242
A + 0.1C_4	0.089	3.817	1.77	18.24	10.29	0.242
A_1	0.153	0.000	3.57	20.10	20.59	0.266
A_1 + 0.1C_1	0.142	2.253	3.25	17.74	18.38	0.266
A_1 + 0.1C_4	0.145	2.085	3.24	17.95	19.40	0.253
A_1+ 2.0C_1	0.058	45.05	1.19	5.91	6.05	0.266
A_2	0.141	0.000	3.22	12.06	12.35	0.266
A_2+ 0.1C	0.135	2.305	2.93	11.24	12.20	0.251
A_2+ 0.1C_3	0.135	2.314	2.93	11.23	12.21	0.251
A_2+ 0.1C_4	0.135	2.309	2.93	11.23	12.20	0.251
A_2+ 0.1C_1	0.131	2.496	2.93	11.17	11.44	0.266
A_2 + 2 C_1	0.056	49.96	1.07	4.65	4.76	0.266
A_2+ 0.1C_2	0.133	1.875	3.04	12.06	12.35	0.266
A_2+ 0.25C_2	0.122	7.739	2.58	12.06	12.35	0.266
A_2+ 0.5C_2	0.107	15.48	2.15	12.06	12.35	0.266
A_2+C_2	0.084	30.95	1.61	12.06	12.35	0.266
A_2+2C_2	0.062	61.91	1.07	12.06	12.35	0.266
A_2+0.1C_5	0.128	3.11	2.93	12.06	12.35	0.266
A_N	0.087	0.000	1.94	20.10	12.30	0.267
A_N+0.1C_5	0.079	5.153	1.76	20.10	10.29	0.266
B	0.073	-	0.00	19.44	10.29	0.000

[a)] Mass ratio of monomers in non-polymerized systems and in mixtures of non-polymerized systems with polymerized inverse microemulsions containing polyacrylamide (acrylamide structural units) particles.

[b)] Concentration of AAm in the system (weight %).

[c)] Molar ratio of toluene (T) and of AOT.

[d)] Molar ratio of water (W) and of AOT.

[e)] Mass ratio of AAm and of water.

microemulsion system at a given polymerization time, t , the polymerization rates

Polymerization kinetics measurements

Dilatometric technique for measuring the polymerization rates in polymerizable dispersion systems was described elsewhere [5]. By derivation of the conversion curves expressing the volume contraction change, ΔV, corresponding to the initial volume V_M of the monomer (e.g. $V_M = V_{AAm}$, valid for polymerization of AAm in the first step of the Two step process) and/or of the oil soluble monomer ($V_M = V_{OSM}$, valid for polymerization of OSM in the second step of the Two step process) in inverse microemulsion system at a given polymerization time, t , the polymerization rates $R_p = (\Delta V / V_M) / \Delta t$ (here t is in minutes) were obtained. For simplification they are given as R_p /a.u./ . For copolymerization of AAm and of OSM (for One step process) the volume change , $V_M = V_{AAm} + V_{OSM}$) corresponds to volume changes of individual polymerizing comonomers. The conversion of monomers (in %) was obtained from the calibration curve expressing the variation of $\Delta V/V_M$ with the gravimetrically determined conversion of the monomers. Values of R_p /a.u./ represent the average of at least four independent measurements. For further details see ref.[11].

Characterization of inverse microemulsions, polymeric products and polymer particles

Viscosity measurements of inverse microemulsions before and/or after polymerization were performed on an Ubbelohde type viscometer at 20 oC. The flow times were compared with the flow times of liquids of known viscosities (mPa s).

For measurements of surface tension of inverse microemulsions, the stalagmometric method was used.

Electrical conductivity of inverse microemulsions were measured on an commercially available Conductivity meter, Type : Ok-102/1, Radelkis Budapest, Hungary.

For phase separation studies of inverse microemulsions calibrated glass vials were used and the volumes of individual phases measured at room temperature for a given time of standing.

Polymer particle sizes were measured by a BI-90 Brookhaven Instrument Corporation particle sizer, employing photon correlation spectroscopy (PCS) of quasi elastically scattered light (QELS). For measurements of the size of polymer particles of the polymerized inverse microemulsion, a sample of polymerized inverse microemulsion, properly diluted by toluene, was used. Polymer particle diameters obtained on dilutions of inverse microemulsion with toluene were extrapolated to zero polymer particle concentration in inverse microemulsion.

Separation of polymeric products from the inverse microemulsions was done by adding excess of ethanol (at least 10 fold volume of the volume of inverse microemulsion). Precipitated crude polymer was freed of emulsifier by addition of excess ethanol for next twelf hrs. Then the new portion of ethanol was used for extraction. This process was repeated about 5 – 7 times till in the extract no AOT emulsifier could be detected (UV spectroscopy) [13]. The extracted polymers were then dried in an oven at 50 °C.

Water and toluene extractions of precipitated and purified polymers obtained from individual polymerized inverse microemulsions were done in glass vessels, similarly to the proces of AOT extraction from the crude polymeric products. The insoluble and soluble parts of individual water and/or toluene extractions were obtained by drying in oven at 50 °C and weighed.

Concentration of AAm structural units in polymeric products was obtained from elementary analysis (nitrogen determination).

Results and Discussion

Characterizations of non-polymerized and polymerized inverse microemulsions and of their mixtures

Selection of the type of polymerized, polyacrylamide containing inverse microemulsion for preparation of modified polyacrylamide particles and choice of the oil soluble monomer for seed polymerization in the presence of polyacrylamide particles were based on our previous results [10,11]. Thus the inverse microemulsion A_2 (Table 1) was selected for seed polymerization of oil soluble monomers.

Data on the water solubility of oil soluble monomers (Table 3) show the relative broad range of the values among individual monomers. Low values of water solubility point at the prevailing partitioning of a given oil soluble monomer in the oil (continuous) phase of inverse microemulsion, while the high values of water solubilities point at the significant partition of the oil soluble monomer also in the disperse water phase of inverse microemulsion. This situation (presence of monomer in minor concentration in an another phase of the dispersion system) influences the course of free-radical polymerization and/or copolymerization of a given monomer and/or comonomer pair (co)polymerization in continuous oil phase and/or in dispersed water droplets (mechanism of solution polymerization of the oil soluble monomer in the continuous oil phase and/or mechanism of inverse microemulsion polymerization, cf ref. [14]).

Table 3. Physical properties of individual components and of their mixtures of inverse microemulsions.

Monomer,M (25 °C) [c]	Density (20 °C) [a] g / cm^3	Refractive indices (20 °C) [b] n_D Monomer	 n_D Polymer	M. sol. in water pph
Methyl acrylate	0.956	1.4020	1.479	5.0
Ethyl acrylate	0.924	1.4060	1.4685	1.5
Butyl acrylate	0.894	1.4180	1.466	0.2
2-Ethylhexyl acrylate	0.8859	1.4360	-	0.01
Methyl methacrylate	0.936	1.4140	1.490	1.52
Styrene	0.9059	1.5470	1.591	0.03 [d]
Acrylamide	1.12	1.4832	-	215.5 [e]
Toluene	0.865	1.4960	-	0.04 [f]
Water	0.998	1.3329	-	-
AOT	1.13	1.4663	-	-
Water/AAm = 0.267(mass)	-	1.365	-	-
A_2 [g]	-	1.4680	-	-

[a] See ref. [16]
[b] See ref. [17]
[c] See ref. [18]
[d] See ref. [19]
[e] Grams per 100 mL of water.
[f] See ref. [20]
[g] See Table 2

As it is well known, the kinetics of polymerization and/or copolymerization, depends on the ratios k_p / $k_t^{0.5}$ (propagation and termination rate coefficients) of individual monomers [21]. On the other hand the copolymerization parameters (r_1 and r_2) of the comonomer M_1 and M_2 couple [22] determine the chemical composition and structure of arising copolymer product This also was considered for proper selection of disperse systems in order to obtain desirable results in the kinetics of the process and structural composition of the obtained modified (co)polymer products.

Solubility parameters of the oil soluble monomers and especially of their polymers with respect to the solubility parameter of the oil (here toluene) phase are important for optimal choice of oil soluble monomer for a given continuous oil phase of inverse microemulsion. The respective values of solubility parameters are given in Table 4. If polymer solubility parameter matches closely the value of solubility parameter of the continuous oil phase, then the polymerization process of the oil soluble monomer in the continuous oil phase of inverse microemulsion has characteristic features of radical polymerization in a good solvent for the arising polymer chains.

Table 4. Solubility parameters of oil soluble monomers, of their polymers and of the continuous /dispersed toluene/water phases of inverse microemulsions [a].

OSM	Monomer (Mpa) $^{1/2}$	Polymer (Mpa) $^{1/2}$
Methyl acrylate	18.2	20.7
Ethyl acrylate	17.6	19.13 (18.21 calc.)
Butyl acrylate	18.2	18.01 (20.42 calc.)
2-Ethylhexyl acrylate		18.45
Methyl methacrylate	18.0	18.58
Styrene	19.0	17.52
Acrylamide [a]		22.8
Toluene	18.2	
Water	47.9	

[a] See ref. [23] .

[b] Value for poly-n-isopropyl acrylamide. No values of solubility parameters were found for acrylamide and/or polyacrylamide.

Some data of acrylamide/polyacrylamide inverse microemulsions before/after polymerization are collected in Table 5. It is interesting, that the viscosity and electrical conductivity of polyacrylamide inverse microemulsion is slightly lower than that of acrylamide (not polymerized) inverse microemulsion. This could be due to the absence of monomer acrylamide in the continuous oil phase of polymerized inverse microemulsion. The addition of oil soluble monomer to polymerized A_2 inverse microemulsion (exemplified by A_2+0.1C_2 system) after polymerization of the system increases remarkably the viscosity. This reflects the presence of dissolved polymer in continuous toluene phase. The electrical conductivity upon addition of oil soluble monomer to polymerized A_2 inverse microemulsion decreases in both (not polymerized and/or polymerized) $A_2+0.1C_2$ systems. Transparency of the polymerized $A_2+0.1C_2$ system decreases in comparison to polymerized A_2 inverse microemulsion.

Table 5. Properties of acrylamide inverse microemulsion A_2 before and/or after polymerization, and of the mixture $A_2 + 0.1\ C_2$ of polymerized (polyacrylamide containing) inverse microemulsion (A_2) with solution of DBP in butyl acrylate (C_2) before and after polymerization of the mixture $A_2 + 0.1\ C_2$ (mass proportion $A_2 + 0.1\ C_2 = 1 : 0.1$). For compositions of individual components of the mixtures see Table 1, for compositions and parameters of the mixture $A_2 + 0.1\ C_2$ see Table 2.

	mPas[a]	µS/cm[b]	n_D[c]	mN/m[d]	App.[e]	d,nm[f]	T(%)[g] / A[h]
A_2							
(Before polymerization)	4.15	5.0	1.468	31.22	c	-	- / -
(After polymerization)	2.25	0.8	1.468	32.0	t,b	25	54.4 / 0.267
polymerization)							
A_2 (polymerized) $+0.1C_2$							
(Before polymerization)	2.10	1.7	1.465	27.18	c(t)	-	- / -
(After polymerization)	13.0	0.5	1.466	28.47	c,b	25	46.2 / 0.338

[a] Viscosity.
[b] Electrical conductivity.
[c] Refractive index.
[d] Surface tension.
[e] Appearance of the system : b – bluish opalescence, c – clear, t – turbid (All single phase Winsor IV dispersions).
[f] Diameter of polymer particles.
[g] Transparency at 520 nm.
[h] Absorbancy at 520 nm.

Appearance of the mixtures $A_2 + 0.1\ C_{OSM}$ (mass proportion A_2 : OSM = 1 : 0.1) of non-polymerized (acrylamide containing) and/or polymerized (polyacrylamide containing) inverse microemulsions A_2 (in amount of 5 g) with added oil soluble monomer OSM (OSM = BA, MMA, EA, MA, S, 2-EHA, in amount of 0.5 g, added step-wise in 0.1 g portions under mixing with magnetic stirrer) on standing (up to 144 hrs) at room temperature before final polymerization of the $A_2 + 0.1\ C_{OSM}$ system, is typical for a single-phase Winsor IV inverse microemulsions.

This observation strongly contrasts with the characters of some of these systems after polymerization (Table 6) and observed phase separation (Table 7). Character of Winsor IV polymerized inverse microemulsions retains only systems with butyl acrylate and styrene (A_2+ $0.1C_2$ and A_2+ $0.1C_9$). Other systems yielded 2-phase and even 3-phase dispersion systems. This means that during polymerization of oil soluble monomer the formed oil soluble polymer can destroy the Winsor IV inverse microemulsion even at low fractions of aqueous phase of inverse microemulsion. The nature of the oil soluble monomers influences mostly the water solubility of individual oil soluble monomers (Table 3). Monomer and polymer solubility parameters are not so differentiated (Table 4). Thus the ability of Winsor IV inverse microemulsion to destruction is connected with the solubility of oil soluble monomer in water (penetration of oil soluble monomer and/or monomer radicals of an oil soluble monomer into the water droplets or water swelled polymer particles of inverse microemulsion, cf. refs. [11,14]).

Table 6. Character and properties of the mixtures $A_2 + 0.1\ C_{OSM}$ (mass proportion A_2 : OSM = 1 : 0.1) of polymerized (polyacrylamide containing) inverse microemulsions (A_2 , amount 5 g) with added oil soluble monomer (OSM = BA, MMA, EA, MA, S, 2-EHA, amount 0.5 g) after polymerization of the OSM in the presence of polyacrylamide particles (polymerization temperature 60°C., polymerization time 4 hrs.).

System				Comments a)		
	OSM	Disperse system	Macrophases	upper	middle	lower
A_2+ $0.1C_2$	BA	Winsor IV	1	-	-	c,b
A_2+ $0.1C_6$	MMA	Winsor I	2	vst	-	t
		on standing 1 month	1	-	-	m
A_2+ $0.1C_7$	EA	Winsor III	3	c	vst	c,b
		on standing 1 month			no change	
A_2+ $0.1C_8$	MA	Winsor I	2	c	-	vst
		on standing 1 month			no change	
A_2+ $0.1C_9$	S	Winsor IV	1	-	-	c,b
A_2+ $0.1C_{10}$	2-EHA		2	c	-	t,p

a) Appearance of the individual phases of the dispersion systems : b - bluish opalescence, c – clear, m - milky , p – precipitated polymer phase, t - turbid , vst - very strongly turbid.

Table 7. Phase separation (separated macrophases are given in vol.% /100) and refractive indexes n_D in some of the studied A_2+ $0.1C_{OSM}$ systems after polymerization [a].

System phase	OSM	Disperse system	upper phase	middle phase	lower
A_2+ $0.1C_2$	BA	Winsor IV	0	0	1
					n_D = 1.466
A_2+ $0.1C_6$	MMA	Winsor I	0.10	0	0.90
		(On standing 1 month	0	0	1
		Winsor IV)			n_D = 1.467
A_2+ $0.1C_7$	EA	Winsor III	0.05	0.45	0.50
		(On standing 1 month)	0.05	0.35	0.60
			n_D = 1.482	n_D = 1.477	n_D = 1.461
A_2+ $0.1C_8$	MA	Winsor I	0.235	-	0.765
		(On standing 1 month)	0.235	-	0.765
			n_D =1.470	-	n_D = 1.470
A_2+ $0.1C_9$	S	Winsor IV	0	0	1
		(No change after 1 month)	0	0	1
					n_D = 1.477
					d = 30 [b]
A_2+ $0.1C_{10}$	2-EHA		0.9	0	0.1 solid
		(No change after 1 month)	n_D = 1.469		

[a] Observation of the systems in closed glass vials as a function of time of standing at room temperature.

[b] Polymer particle diameter in nanometers.

Some qualitative evaluation is possible on the basis of measured refractive indexes. Taking into account the values of refractive indexes of individual components of inverse microemulsions (Table 3), the appearance of the inverse microemulsions after polymerization (Table 6), and observed values of refractive indexes of separated phases of inverse microemulsions (Table 7), the following conclusions may be presented. The polymerized inverse microemulsion A_2 (main component is toluene) definitely determines the refractive index of the A_2+ $0.1C_{OSM}$ disperse systems (cf. the values of n_D for A_2 = 1.4680 vs. the values of A_2+ $0.1C_{OSM}$ single-phase disperse system of Winsor IV type (for OSM=BA, S) the respective values are n_D = 1.466 and 1.477. Similarly for two-phase systems (OSM= MMA, MA , 2-EHA) the respective values are n_D = 1.467 (lower milky phase), 1.470 (lower very strongly turbid phase and upper clear phase), 1.469 (upper clear phase, lower phase contains precipitated polymer, n_D was not measured). Three-phase system (OSM= EA) was formed by upper clear phase (n_D = 1.482), middle, very strongly turbid phase (n_D = 1.477) and bottom clear, bluish phase (n_D = 1.461). Here the upper, oil phase contained part of AOT dissolved in toluene. The middle phase contained unreacted EA (very low conversion of EA, cf. Table 9) and the bottom phase is w/o microemulsion containing polyacrylamide particles partly modified by EA and homopolymer polyethylacrylate (assumed according to the analysis of the polymeric product discussed later on the example of A_2 +0.1 C_2 (BA) system). More details on the analysis of the A_2 +0.1 C_7 (EA) system will be presented in other paper (ref. [24]).

Polymerization rates of oil soluble monomers in the presence of polyacrylamide particles in inverse microemulsions

With respect to homopolymerization rate of acrylamide in inverse microemulsion A_2, the polymerization rates of oil soluble monomers in the presence of polyacrylamide particles of inverse microemulsion A_2 are smaller by several orders (Table 8). The polymerization rates of oil soluble monomers in the presence of polyacrylamide particles decrease in the order

BA > EA > MA > 2EHA > MMA > S

which does not correspond strictly with the ordering of their $k_p / k_t^{0.5}$ values [21] :

$$\begin{array}{llllll} MA > & EA > & 2\text{-}EHA \approx & BA > & MMA > & S \\ 84.0 & 60.6 & 32.1 & 26.9 & 15.6 & 2.35 \text{ all } \times (10^{-2}\ \text{mol}^{-0.5}\ \text{dm}^{1.5}\ \text{s}^{-0.5}). \end{array}$$

The highest polymerization rate ($R_{p\ max}$ / (a.u.)) for BA and S was found at conversion of monomer below 3 %, the highest polymerization rates of other oil soluble monomers were achieved at conversions 4.43 (MMA), 7.32 (MA), 8.80 (2-EHA), and 17.38 (EA) . It is interesting to note, that for ideal course of free-radical polymerization in solution (in the absence of gel effect) the maximum rate of polymerization is the polymerization rate close to zero conversion (determination of the polymerization rate at zero conversion of monomer). This condition closely fulfil S and BA. The other monomers decline from the ideal course of polymerization in solution and thus the mechanism of polymerization is not given by pure homopolymerization of oil soluble monomer in the continuous phase. This is clearly documented by the value of maximum polymerization rate for other monomers and notably for polymerization of water soluble monomer acrylamide in water droplets of inverse microemulsion, where the mechanism of inverse microemulsion polymerization applies [3].

Table 8. Maximum homopolymerization rates R_p (a.u.) of the oil soluble monomer OSM (OSM= C_2 (BA), C_6 (MMA), C_7 (EA), C_8 (MA), C_9 (S), C_{10} (2-EHA)) in the mixtures $A_2+0.1C_{OSM}$ of polyacrylamide containing inverse microemulsion A_2 with OSM containing systems. For compositions and parameters characterizing the individual non-polymerized systems, the polymerized inverse microemulsion A_2, and of their mixtures see Tables 1 and 2. Polymerization temperature 60 °C.

System	OSM	$R_{p,max}$ (a.u.) / C% [a)]	C_{FIN}% / min.[b)]
A_2[c)]	-	0.09104 / 36.70	84.83 / 73.2
$A_2+0.1C_2$	BA	0.00181 / 2.0	96.00 / 412.0
$A_2+0.1C_6$	MMA	0.00023 / 4.43	28.16 / 436.0
$A_2+0.1C_7$	EA	0.00087 / 17.38	75.75 / 280.0
A_2[d)] $+0.1C_7$	EA	0.01880 / 11.47	98.65 / 145.5
$A_2+0.1C_8$	MA	0.00048 / 7.32	59.84 / 426.0
$A_2+0.1C_9$	S	0.00004 / 1.85	7.72 / 325.0
$A_2+0.1C_{10}$	2-EHA	0.00037 / 8.80	90.00 / 400.5

[a)] Maximum rate of AAm polymerization in arbitrary units (see Experimental part) .
[b)] Conversion at which polymerization was stopped.
[c)] Data refer to polymerization of AAm in inverse microemulsion not containing OSM (see Table 1)
[d)] Non-polymerized acrylamide containing inverse microemulsion A_2 was used. The system represents the case of simultaneously proceeding (co)polymerization of AAm and EA.

The effect of reaction conditions (OSM/AAm mass ratio) on the kinetics of OSM polymerization in the presence of polyacrylamide particles and on the character of the formed disperse system is shown in Table 9. For this study the polymerization of BA in the systems $A_2 + y\ C_2$ (y ranged between 0.1 and 2) was selected.

The character of BA containing system, which was used (inverse microemulsion, solution, or bulk monomer) for preparation of the reaction systems, did not significantly influenced the results obtained (rate of polymerization of oil soluble monomer, character of formed polymer product). The increasing of the concentration of an oil soluble monomer (ratio BA/PAAm) in the reaction system, however, influenced profoundly the polymerization rate of BA as well as the character of obtained products. Thus for A_2+C_2 system the maximum polymerization rate varied between 0.0018 (a.u.) and 0.100 (a.u.) (for $A_2+0.1C_2$ and A_2+2C_2). The resulting disperse system was either typical single phase inverse microemulsion or turbid, very viscous (or even toluene and/or monomer swelled solid, according to the conversion of BA), single phase dispersion system composed from the dispersed water swelled polyacrylamide particles in the poly(butyl acrylate) matrix.

Table 9. Maximum homopolymerization rates of acrylamide in the acrylamide containing inverse microemulsions (A, A_1, A_2, A_N), butyl acrylate in the butyl acrylate containing inverse microemulsion (B), and/or butyl acrylate in the mixtures of polymerized acrylamide containing inverse microemulsions (A, A_1, A_2, A_N) with butyl acrylate containing systems (B , C , C_1 , C_2 , C_3 , C_4 , C_5), polymer particle size and appearance of final disperse systems. For compositions and parameters characterizing the individual non- polymerized systems and polymerized inverse microemulsions and of their mixtures see Tables 1 and 2. Polymerization temperature 60 °C.

System	$R_{p,max}$ (a.u.)/C% [a]	C_{FIN}%/min.[b]	d_n /nm [c]	Appearance [d]
A	0.1232/13.8 [e]	92/116	31	c,b
A+ B	< 0.0001	<10/300	30	c
A+0.1C	0.0006/2.5	64/440	40	c
A+0.1C_3	0.0007/2.4	52/496	32	c
A+0.1C_4	0.0006/7.5	84/470	31	c,b
A_1	0.1329/22.7 [e]	96/113	95 [f]	c,b
A_1 + 0.1 C	0.0006/10.1	81/321	-	c,b
A_1 + 0.1 C_1	0.0007/10.0	93/381	68	c,b
A_1 + 2.0 C_1	0.0079/3.3	11/227	-	t,vv
A_1 + 0.1 C_3	0.0007/2.4	73/310	-	c,b
A_1 + 0.1 C_4	0.0008/12.4	92/384	83	m
A_2	0.1284/18.6 [e]	93/91	36	c,b
A_2+0.1C	0.0008/11.9	62/192	43	c,b
A_2+0.1C_3	0.0010/2.5	53/122	45	c,b
A_2+0.1C_4	0.0007/7.0	53/305	32	c,b
A_2+0.1C_1	0.0014/2.0	91/424	36	c
A_2+2C_1	0.0129/8.0	51/117	-	j
A_2+0.1C_2	0.0018/2.0	96/412	(40)	c,b
A_2+0.25C_2	0.0023/17.1	95/295	-	t,v
A_2+0.5C_2	0.0087/45.0	-	-	vv
A_2+C_2	0.0083/26.0	71/118	-	vv
A_2+2C_2	0.0100/18.5	25/16	-	t,vv
A_2+0.1C_5	0.0037/1.27	-	30	c,b
A_N	0.0340/15.71	-	28	c
B	0.0002/2.33 [e]	<5/450	-	c

[a] Maximum rate of AAm polymerization in arbitrary units (see Experimental part) .

[b] Conversion at which polymerization was stopped.

[c] Number average diameter of polymer particles, obtained by extrapolation to zero concentration of polymer particles (sample diluted by toluene).

[d] Appearance of the dispersion system after polymerization: c- water clear , b – bluish opalescence , j – jelly- like , m – milky , p – polymer precipitate , t – turbid , vv – very viscous.

[e] Average value of four measurements.

[f] Value not extrapolated to zero polymer particle concentration..

Modified polymer products characterization

For preparation of modified polyacrylamide particles in Winsor IV disperse systems the polymerized polyacrylamide inverse microemulsion of the type A_2 and oil soluble monomers in weight proportions 1 : 0.1 (disperse systems $A_2 + 0.1C_{OSM}$) were analyzed for acrylamide content in final polymer products obtained by precipitating crude polymer products from disperse system upon addition of excess of ethanol and following extractions by ethanol (removing of AOT surfactant).

Table 10. Calculation of the conversions of acrylamide (% C_{AAm}) and of the oil soluble monomer (% C_{OSM}) from the concentration of acrylamide structural units (% AAm_P , average value of two measurements) in polymer product obtained in the polymerization of the mixture $A_2 + 0.1\ C_{OSM}$ of polymerized inverse microemulsion (A_2) with a solution of dibenzoyl peroxide in an oil soluble monomer (OSM = BA, MMA, EA, MA, S).

System	OSM	% N_2	% AAm_P	% C_{AAm}		% C_{OSM}	
				a)	b)	c)	a)
$A_2 + 0.1\ C_2$	BA	10.74355	54.52	77.11	44.49	41.00	34.31
$A_2 + 0.1\ C_6$	MMA	8.49140	43.09	72.71	70.44	64.92	51.21
$A_2 + 0.1\ C_7$	EA	14.50266	73.60	42.10	19.13	17.63	80.54
$A_2 + 0.1\ C_8$	MA	7.94436	40.32	72.29	78.94	72.75	57.06
$A_2 + 0.1\ C_9$	S	11.20007	56.84	88.55	40.50	37.32	35.86
$A_2 + 0.1\ C_{10}$	2-EHA	2.38443	12.10	25.61	> 100	> 100	99.23

[a] Calculated from the known quantity of determined concentration of AAm_P (%) and OSM_P (%) ($OSM_P = 100 - AAm_P$) in the purified polymer product (after extractions in ethanol), known amounts (G_D , grams)and compositions (AAm_0 , OSM_0 , grams) of the feed and of polymer product (PPr , grams). For calculation (e.g. for system $A_2 + 0.1\ C_9$) the following equation was used :

$\%\ C_{OSM} / 100 = \mathrm{PPr}\ (100 - AAm_P) / OSM_0 \times G_D = 2.963 \times (100 - 56.84) / 5.7 \times 62.56 =$
$= 0.3586$

$\%\ C_{AAm} / 100 = \mathrm{PPr} \times AAm_P) / AAm_0 \times G_D = 2.963 \times 56.84 / 3.04 \times 62.56 = 0.8855$

[b] Calculated from the determined concentration of AAm_P in reaction product and from the content of acrylamide (AAm_0 , see Table 2 and $A_2 + 0.1\ C_X$, for x = 2, 6 - 10) and of the oil soluble monomer (OSM_0 , see Table 2 and $A_2 + 0.1\ C_X$) in the feed and for 100 % conversion of AAm in polymerized AAm containing inverse microemulsion. Thus for $A_2 + 0.1\ C_2$ system the conversion of BA was $\%\ C_{BA} = (100 - \%\ AAm_P) \times AAm_0 \times 100 / \%\ AAm_P \times BA_0\ (100 - 54.52) \times 3.04 \times 100 / 54.52 \times 5.7 = 44.49\ \%$.

[c] Values of % C_{OSM} calculated in method [a] were multiplicated by the value of experimentally determined conversion of acrylamide in inverse microemulsion A_2 (92.16 %). Thus for conversion of BA = 44.49 % after correction for the experimental value of AAm conversion the value 41.00 % (= 44.49 % x 0.9216) was obtained for conversion of butyl acrylate.

As can be seen from Table 10 (for colloidal properties and behavior of systems studied see Tables 6 and 7) polymer products with different concentration of AAm structural units were obtained. The results presented here need no further comments, perhaps except the percent conversion of acrylamide. The experimentally determined conversion of acrylamide in inverse microemulsion which was used for seed polymerization of OSM in inverse microemulsion was 92.16 %. Thus the lower values of conversions of AAm in products obtained by seeded polymerizations of OSM in the presence of polyacrylamide particles of A_2 inverse microemulsion could be due to partial loss of acrylamide containing polymer products in processes of separation and extraction of polymeric products from inverse microemulsions. AOT surfactant participates (tertiary hydrogens in 2-ethylhexyl chains of AOT) in transfer reactions with polymer radicals [25] and formed AOT radical can then participate in radical reactions in the system and thus to be incorporated (by termination and addition reactions) in polyacrylamide containing products. The latter can then be extracted in purification and/or separation processes and thus to be lost in reasonable amounts from the system (see systems with 2-EHA and EA). Calculated conversions of OSM (2-EHA) over 100 % are unrealistic and confirm that in this case the supposition of 100 % (or even of determined 92.16 %) conversion of AAm (and thus of the amount of polyacrylamide formed in inverse microemulsion used for seeded polymerization of an oil soluble monomer) can not be used for calculation of OSM monomer conversion.

The results obtained (Tables 7, 9) were used for final choice of the oil soluble monomer(s) as component(s) in inverse microemulsion A_2 . Thus the systems A_2 + 0.1 C_2 (BA) and A_2 + 0.1 C_9 (S) were used for preparation and analysis of butyl acrylate and/or styrene modified polyacrylamide particles in inverse microemulsions and disperse systems (Table 11).

Polymer products, which were obtained by seeded butyl acrylate and/or styrene polymerizations in the presence of polyacrylamide particles after extractions in water or toluene, were copolymers of [AAm/BA] and/or [AAm/S] (here AAm, BA and S mean structural units of individual monomers in copolymers) and homopolymers. Water- and toluene insoluble products represent only copolymer products (for both BA and S seeded polymerizations), water soluble parts may contain part of seed polyacrylamide besides [AAm/BA] and [AAm/S] copolymers. Homopolymers of oil soluble monomers were detected in toluene soluble part only in the case of butyl acrylate seeded polymerization. In the case of copolymerization of AAm and S besides copolymers [AAm/S] in water- and/or oil insoluble parts also homopolymers of AAm (9.4 %) and S (1.4 %) as water-soluble and/or toluene soluble parts of polymer products were found. Presence of styrene homopolymer in toluene soluble part of seeded S polymerization is probably very low due to slow homopolymerization rate of S in continuous oil phase (cf. value 1.4 % of S homopolymer found in toluene soluble part of AAm and S copolymerization in inverse microemulsion).

Table 11. Results of selective extractions by water and/or toluene of the polymeric product containing 54.52 mass % of AAm structural units obtained in the polymerization of the mixture $A_2 + 0.1\ C_2$ of polymerized inverse microemulsion (A_2) with a solution of dibenzoyl peroxide in butyl acrylate (C_2) and/or of the polymeric product containing 56.84 mass % of AAm structural units obtained in the polymerization of the mixture $A_2 + 0.1\ C_9$ of polymerized inverse microemulsion (A_2) with solution of dibenzoyl peroxide in styrene (C_9). The polymeric products and the separated insoluble and soluble parts of the polymeric products were analyzed for acrylamide structural units (nitrogen content, elementary analysis). For recipes see Table 1 and Table 2. For comparison are given values found for polymeric product obtained in the copolymerization of acrylamide with styrene in inverse microemulsion.

	Water extraction[a]		Toluene extraction[a]	
	Insol.part	Soluble part	Insol.part	Soluble part
AAm/BA[b]				
% product	82.03 AAm/BA	17.97 AAm/BA	85.30 AAm/BA	14.70 BA[c]
% AAm	54.10	33.19	60.63	0.00
AAm/S[b]				
% product	37.18 AAm/S	62.82 AAm/S	73.40 AAm/S	26.60 AAm/S
% AAm	24.83	75.17	71.78	28.22
(AAm+S)[d]				
% product	89.2 AAm/S	9.4 AAm[3]	98.6 AAm/S	1.4 S[3]
% AAm	68.7	100.0	72.2	0.0

[a] For balance mass studies see Appendix

[b] Copolymer AAm/BA and/or AAm/S.

[c] Homopolymer BA and/or S

[d] Copolymerization of AAm and S in inverse microemulsion: T/S/AOT/W/AAm/APS ; S/AAm = 1.25 ; AAm/W = 0.267 ; [W] / [AOT] = 10.29 ; $\Phi_{aw} = 0.083$; [APS] =30.4 mmol/L of water. Data taken from Ref. [14].

Conclusions

It was shown that the polymerization of an oil soluble monomer in inverse microemulsion containing polyacrylamide particles led to the formation of modified polymer products in high yield. Depending on the ratio polyacrylamide) / oil soluble monomer of the inverse microemulsion system the polymerized reaction product is in the form of water swollen polymer particles composed of (co)polymer containing AAm/oil soluble monomer structural units and of AAm homopolymer, dispersed in continuous oil phase, or in the form of a viscous, or even solid mixture of water swelled (co)polymer of AAm/oil soluble monomer and of AAm homopolymer containing particles, dispersed in the continuous oil phase formed by non-polymerizing solvent or in homopolymer of the oil soluble monomer (continuous phase of the feed was formed by oil soluble monomer only, no non-polymerizing solvent was added). In all cases macroscopically single-phase systems were obtained.

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Appendix

Balance mass studies :

Product AAm/BA

% wt of AAm : 82.03 x 0.541 + 17.97 x 0.3319 = 50.34 % , cf. 54.52 % , i.e. difference 4.18 % (water extraction).

% wt of AAm : 85.30 x 0.6063 = 51.72 % , cf. 54.52 , i.e. difference 2.80 % (toluene extraction).

Product AAm/S

% wt of AAm : 37.18 x 0.2483 + 62.82 x 0.7517 = 56.45 % . cf. 56.84, i.e. difference 0.39 % (water extraction).

% wt of AAm : 73.40 x 0.7178 + 26.60 x 0.2822 = 60.19 % , cf. 56.84 % , i.e. difference 3.35 % (toluene extraction).

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