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Acrylamide and Butyl Acrylate Polymerization in Winsor IV (w/o) and Winsor I (o/w) Microemulsions

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ABSTRACT: The preparation of toluene-based single-phase Winsor IV water-in-oil (w/o) inverse microemulsions containing the (co)monomer couple acrylamide (AAm)/butyl acrylate (BA), their transformation to the two-phase Winsor I (oil-in-water (o/w) microemulsion phase + excess of oil phase) microemulsion and homo- and (co)polymerization of (co)monomers initiated by ammonium peroxodisulfate in both types of microemulsions were studied. Increasing of the volume fraction of aqueous phase, $\Phi_{aw,}$ of the parent single-phase Winsor IV w/o inverse microemulsion by addition of solution of AAm in water led first only to the increase of AAm monomer concentration in inverse microemulsion, and finally to the formation of a two-phase Winsor I o/w microemulsion. Thus, Winsor IV and Winsor I microemulsions characterized with 3-fold and 6-fold higher content of AAm (i.e., up to 6 mass % in Winsor IV and 12 mass % in the microemulsion phase of Winsor I with respect to only 2 mass % in the parent Winsor IV w/o microemulsion) were obtained. Maximum rate of (co)polymerization of AAm/BA couple in Winsor IV w/o inverse microemulsion is only 1.5 times greater than that found for o/w microemulsion phase of Winsor I. Maximum homopolymerization rate of BA in toluene-based Winsor IV inverse w/o microemulsion in comparison to BA-based Winsor IV inverse w/o inverse microemulsion is only 1/75 of the maximum rate of BA homopolymerization in the latter system. The kinetic behavior of AAm and BA (co)monomer pair in free-radical polymerization in studied microemulsions was explained as a result of the different monomer partition between water and oil phases of the dispersion system, of the capability of monomer and/or oligomer radical formation in the individual phases, and of the transfer of these radicals between individual phases of the w/o and/or o/w microemulsions.

Introduction

Free-radical polymerization of water-soluble monomers in inverse microemulsions was studied in many papers, cf. refs 1−5. The aim of these studies was to elucidate the kinetics and mechanism of the homopolymerization process, the mechanism of polymer particle formation and growth, and the determination of the properties of polymer particles in polymerized inverse microemulsion.

The simultaneous polymerization and copolymerization of monomers differing reasonably in their water solubilities in water in oil (w/o) dispersions were also studied.[6,7] The kinetic study of the effect of the oil-soluble monomer styrene located in the continuous oil phase on the acrylamide polymerization in inverse microemulsion pointed to an effective competition between the monomers in the oil phase (slow homopolymerization of styrene and/or (co)polymerization of styrene with acrylamide dissolved in the oil phase) and the monomers in the water pools of inverse micelles (rapid homopolymerization of a major part of acrylamide) for initiator radicals and/or (co)oligomer radicals.[8−10]

The essential problem in the preparation of a monomer-containing inverse microemulsion as a medium for a free-radical polymerization is the stability of the inverse microemulsion before and during the polymerization of the monomer. Several attempts were reported on the optimization of the process of inverse microemulsion formation at higher monomer contents and at lower emulsifier concentrations.[11−13] We have shown[14] that stepwise addition of water to the macroscopically single-phase Winsor IV (w/o, water-in-oil) inverse microemulsion toluene/AOT (sodium bis(2-ethylhexyl) sulfosuccinate)/water/AAm may lead to the formation of a two-phase Winsor I system. (Winsor IV relates to the macroscopically single-phase (w/o or o/w, oil-in-water) microemulsion, and Winsor I relates to the two-phase o/w microemulsion which is composed from o/w microemulsion (lower phase) and oil (upper phase). For further details of the Winsor's nomenclature of microemulsions, cf. ref 15). It was also shown[16] that the addition of sodium dodecyl sulfate (SDS) to the aqueous phase of the inverse microemulsion toluene/AOT/water/AAm/SDS increases the value of the volume fraction of aqueous phase, Φ_{aw}, necessary for the formation of the two-phase microemulsion.

This paper relates to the preparation of water-soluble, hydrophilic, AAm monomer and oil-soluble, lipophilic, BA monomer containing dispersion systems having toluene- or mixture of toluene with oil-soluble monomer as continuous oil phase and the polymerization of monomers in these dispersion systems. The reason for this choice of monomers was that they constitute the hydrophilic/lipophilic (co)monomer couple AAm/BA enabling the preparation of partly hydrophobized polymer particles.This (co)monomer couple has the ratio of propagation k_p and termination k_t rate coefficients $(k_p/k_t^{0.5})_{AAm}/(k_p/k_t^{0.5})_{BA}$ close to 2,[17] and thus from this point of view, the BA monomer should have a significantly lower impact on the overall polymerization kinetics in comparison to that what was found in the case of previously studied (co)monomer couple AAm/styrene (here the ratio of the rate coefficients is over 200[8]).

The aim of this paper was to find the optimal composition of aqueous phase for acrylamide and butyl acrylate containing polymerizable inverse microemulsions of the Winsor IV (w/o) type, enabling the formation of single-phase Winsor IV microemulsions characterized by values of [T]/[AOT] between 10 and 20 and by high

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Φ_{aw} values (up to 0.50). This should enable the formation of single-phase Winsor IV w/o microemulsions with relatively high concentration of water-soluble AAm monomer prior to their transformation to a two-phase Winsor I o/w microemulsion. Next task was to determine the rates of homo- and (co)polymerization of AAm and BA in Winsor IV (w/o) and in the microemulsion phase of Winsor I (o/w) dispersion systems. The results should bring new knowledge on the mechanism of polymerization and of polymer particles' formation in microemulsions containing (co)monomers differing in their lipophilic/hydrophilic properties. They should also help for formulation of optimalized recipes of polymerizable microemulsions for the preparation of nanosized (co)-polymer particles of various degree of hydrophilicity.

Experimental Part

Chemicals. Acrylamide (AAm) (puriss., recrystallized; from Serva, Feinbiochimica, GmbH and Co., Heidelberg, Germany), sodium bis (2-ethylhexyl) sulfosuccinate (AOT) (purum; from Fluka Chemie AG, Buchs, Switzerland), sodium dodecyl sulfate (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 Republic) was recrystallized from ethanol. Commercially available butyl acrylate (BA) (purum; from Merck-Schuchardt, Hohenbrunn/München, Germany) was deprived of inhibitor by distillation under a 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. The parent polymerizable inverse microemulsions containing less than 10 vol % (i.e $\Phi_{aw} < 0.1$) of aqueous phase were prepared simply by mixing solutions of AOT in toluene/ butyl acrylate and/or butyl acrylate with water solution of acrylamide and/or acrylamide and sodium dodecyl sulfate at room temperature. In the preparation of inverse microemulsions for polymerization experiments, the water-soluble initiator APS was added to the water solution of acrylamide and/or to the water solution of acrylamide and sodium dodecyl sulfate.

For preparation of dispersion systems with higher content of the aqueous phase ($\Phi_{aw} > 0.1$), the above-mentioned AAm/BA inverse microemulsions were titrated with water, with a solution of AAm in water and/or with a solution of AAm and SDS in water. Here and afterward, under the titration process is meant the stepwise addition of ca. 0.1−0.2 mL amounts of aqueous phase to the 10 mL of parent, single-phase, water clear, inverse microemulsions under gentle stirring. The microemulsion after every addition of the amount of aqueous phase was then left to rest at least for 30 min and then visually observed. If no phase separation occurred, the whole process was repeated until turbidity evolved and/or the phase separation was observed.

The dilatometric technique for measuring the polymerization rates in polymerizable dispersion systems was described elsewhere.[8,14] By derivation of the conversion curves expressing the volume contraction change, ΔV, corresponding to the initial volume of AAm and BA in inverse microemulsion system, V_M, ($V_M = V_{AAm} + V_{BA}$) at a given polymerization time, t, the polymerization rates $R_p = \Delta V/(V_{AAm} + V_{BA}) \times 1/\Delta t$ (t is in minutes) were obtained. For simplification they are given as R_p/au. 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.

Limiting viscosity numbers of poly(butyl acrylate) were measured in acetone at 25 °C and the viscosity-average molecular weights were calculated[18] from the equation $[\eta] = 6.85 \times 10^{-5} M_v^{0.75}$.

Table 1. Titration of AAm/BA Winsor IV (w/o) Inverse Microemulsion T (14.5 g)/BA (0.5 g)/AOT(3.6 g)/Water (1.5 g)/AAm (0.4 g)/ SDS, ([T]/[AOT] = 19.4) by Distilled Water and Its Visual Characterization (Temperature 20 °C)

AOT/SDS	SDS, g	Φ_{aw}[a]	appearance[b]
	0.0000	0.083	c
		0.132	c
		0.146	t
		0.155	2
36	0.1000	0.087	c
		0.173	c
		0.179	t
		0.193	2
17	0.2120	0.092	c
		0.226	c
		0.242	t
		0.258	2
10.7	0.3353	0.097	c
		0.235	c
		0.256	t
		0.265	2

[a] Volume fraction of aqueous phase (volumes of water,AAm, and SDS) in dispersion system, i.e., Φ_{aw} = aqueous phase/(aqueous phase + oil phase). Oil phase (volumes of toluene, butyl acrylate, and AOT). [b] Appearance: c, clear; t, turbid; 2, two-phase Winsor I (o/w) system.

Table 2. Titration of AAm/BA Winsor IV (w/o) Inverse Microemulsion T (14.5 g)/BA (0.5 g)/AOT(3.6 g)/Water (1.5 g)/AAm (0.4 g)/SDS (0.100 g), ([T]/[AOT] = 19.4) by Water (A), Water and AAm (B), Water and SDS (C), and Water, AAm, and SDS (D) and Its Visual Characterization (Temperature 20 °C)

	Φ_{aw}			
A	B	C	D	appearance[a]
0.087	0.087	0.087	0.087	c
0.173	0.199	0.206	0.192	c
0.179	0.257	0.257	0.226	t
0.193	0.313	0.275	0.395	2

[a] Appearance: c, clear; t, turbid; 2, two-phase Winsor I (o/w) system.

Results and Discussion

The titration of the parent toluene/BA/AOT/water/AAm/SDS inverse microemulsion by water clearly shows that the presence of SDS in the inverse microemulsion increases the value of Φ_{aw2} necessary for the formation of the two-phase Winsor I system (Table 1). Addition of water to parent inverse microemulsion decreases inevitably the concentration not only of the oil components but also of the acrylamide and/or SDS in the dispersion system. This, of course, is not desirable situation for several reasons, e.g., a very low PAAm concentration in the polymerized inverse microemulsion. This drawback can be avoided by titration of the inverse microemulsion by a water solution of AAm and/or by a water solution of AAm and of SDS. Here the mass ratios AAm/water and SDS/water are not changed during titration of the inverse microemulsion system (see later). Comparison of results presented in Table 2 clearly points at the titration system D (for titration was used a water solution of AAm and SDS) as the best, because it offers for the formation of a two-phase system the highest value of Φ_{aw2}.

Detailed characteristics of the Winsor IV (w/o) inverse microemulsions differing by their [Toluene]/[AOT] values, in the course of their transformation to a two-phase system is presented in Tables 3 and 4. For both cases the titration system D was used. Increasing Φ_{aw} changes profoundly the composition of the dispersion systems.

Table 3. Characteristics (Volume Fraction of the Aqueous Phase, Φ_{Aw}, Mass Ratios of BA/AAm, AOT/SDS, % AAm, and Appearance) of Inverse (w/o) Winsor IV Microemulsion T (14.5 g)/BA (0.5 g)/AOT (3.6. g)/Water (1.5 g)/AAM (0.4 g)/SDS (0.1000 g) ([T]/[AOT] = 19.4) before and during Its Transformation to Winsor I (o/w) Dispersion, Titrated by a Solution of AAm (0.4 g) and SDS (0.05 g) in Water (1.5 g)

Φ_{aw}	BA/AAm	% AAm[a]	AOT/SDS	appearance[b]
0.087	1.250	1.63	36.00	c
0.192	0.494	3.86	20.42	c
0.214	0.452	4.15	19.14	c
0.226	0.401	4.58	17.50	t
0.244	0.380	4.79	16.78	t
0.285	0.304	5.68	14.08	m,v
0.326	0.242	6.70	11.67	m,v
0.343	0.224	7.06	10.94	m
0.354	0.213	7.31	10.47	m
0.389	0.183	8.04	9.21	2
0.395		0.00		2[c]
0.395		11.80	5.28	2[d]

[a] Total content of AAm (grams per 100 mL of the dispersion system). [b] Appearance: c, clear; t, turbid; v, viscous; m, milky; 2, two-phase Winsor I system. [c] Winsor I o/w microemulsion,data for separated upper (oil) phase. [d] Winsor I o/w microemulsion,data for separated bottom (microemulsion) phase.

Table 4. Characteristics (Volume Fraction of the Aqueous Phase, Φ_{Aw}, Mass Ratios of BA/AAm, AOT/SDS, % AAm, % BA and Appearance) of Inverse (w/O) Winsor IV Microemulsion T (14.5 g)/BA (0.5 g)/AOT (6.0 g)/Water (1.5 g)/AAM (0.4 g)/SDS (0.2120 g) ([T]/[AOT] = 11.6) before and during Its Transformation to Winsor I (o/w) Dispersion, Titrated by a Solution of AAm (0.4 g) and SDS (0.05 g) in Water (1.5 g)

Φ_{aw}	AAm[a]	AOT/SDS	BA/AAM	%BA[b]	appearance[c]
0.084	1.62	28.30	1.250	54.59	c
0.243	4.98	17.32	0.337	25.21	c
0.351	7.25	12.63	0.199	16.60	b
0.364	7.54	12.14	0.187	15.75t	t
0.397	8.24	10.99	0.162	13.94	t
0.401	8.33	10.86	0.159	13.72	t
0.417	8.65	10.38	0.149	12.97	tv
0.431	8.96	9.94	0.141	12.36	t(v)
0.435	9.03	9.84	0.139	12.20	t
0.451	9.39	9.34	0.129	11.43	c
0.491	10.22	8.26	0.110	9.91	c
0.494	10.28	8.19	0.109	9.83	m →2

[a] Total content of AAm (grams in 100 mL of the dispersion system). [b] Mass percent of BA in the mixture with AAm. [c] Appearance: c, clear; b, clear with bluish opalescence; t, turbid; v, viscous; m → 2, initially milky dispersion system on standing formed a two-phase Winsor I system.

As expected, a lower Φ_{aw2} value (0.389) for system with [toluene]/[AOT] = 19.4, AOT/SDS = 9.21, and AAm = 8.04% was obtained. The corresponding values of Φ_{aw2} = 0.494, AOT/SDS = 8.19, and AAm = 10.28% were obtained for a system with a higher concentration of AOT ([toluene]/[AOT] = 11.6). For the latter system, the results of visual characterization (transparency of the system observed between $\Phi_{aw} = 0.451-0.491$) point to the existence of an unstable multiple dispersion system of w/o/w structure,[19,20]which upon slight change of the composition of the system from $\Phi_{aw} = 0.491$ to Φ_{aw2} = 0.494 transformed itself into a two-phase Winsor I dispersion.

The increase of the macroviscosity of the dispersion system between $\Phi_{aw} = 0.285$ and $\Phi_{aw} = 0.326$, first observed already in refs 14 and 21 can be a result[22]of a spheres → rods transition (Table 3). The more pronounced increase of the macroviscosity in the case of dispersion system characterized by the value of [T]/[AOT] = 11.6 between $\Phi_{aw} = 0.417$ and $\Phi_{aw} = 0.431$ reflects probably the tranformation of Winsor IV (w/o) to a bicontinuous Winsor IV dispersion system[23] (Table 4).

Table 5. Compositions (Mass %) of the Winsor IV (w/o) Inverse Microemulsion, Water Solution of AAm and SDS (WAS), and Oil and Microemulsion Phases of the Winsor I (o/w) Dispersion System[a])

components	Winsor IV	WAS	Winsor I (oil phase)[b]	Winsor I (microemulsion phase)
toluene	70.39		100.00	23.27
butyl acrylate	2.43			2.16
AOT	17.48			15.57
water	7.28	75.00		44.25
AAm	1.94	20.00		11.80
SDS	0.49	5.00		2.95

parameters	Winsor IV	WAS	Winsor I (oil phase)[b]	Winsor I (microemulsion phase)
Φ_{aw}	0.087	1.000	0.000	0.573
water/AAm	0.267	0.267		0.267
BA/AAm	1.25			0.183
[T]/[AOT]	19.4			7.21
[water]/[AOT]	10.3			7.0
SDS/water	0.067	0.067		0.067
AOT/SDS	36			5.3

[a] A 40 mL aliquot of inverse microemulsion T (14.5 g)/BA (0.5 g)/AOT (3.6 g)/water (1.5 g)/AAm (0.4 g)/ SDS (0.100 g) was titrated by 19.6 mL of the solution of AAm (0.4 g) and SDS (0.100 g) in water (1.5 g). Winsor I dispersion system consisted of an oil phase (16.27 g) and a microemulsion phase (42.89 g). [b] Traces of water and/or BA were neglected (see Results and Discussion).

The composition and compositional parameters of the parent Winsor IV w/o toluene-based inverse microemulsion and of the (by titration) generated two/phase (o/w) Winsor I inverse microemulsion are presented in Table 5. The latter was composed from the oil phase (16.27 g, i.e., 27.54 mass %) and from the o/w microemulsion phase (42.89 g, i.e., 72.46 mass %). Although the microemulsion phases of the both dispersion systems (i.e., Winsor IV and Winsor I) have the same values of water/AAm and SDS/water, they differ in [T]/[AOT], [water]/[AOT], AOT/SDS, BA/AAm, and Φ_{aw}parameters. The inverse (w/o) Winsor IV microemulsion contains only 1.94 mass % of AAm, but the (o/w) microemulsion phase of the Winsor I contains 11.80 mass % of AAm.

Results of the determination of homo- and (co)-polymerization rates of AAm, BA and AAm/BA couple in Winsor IV (w/o) and Winsor I (o/w) microemulsions are presented in Table 6. The highest rates were observed for AAm homopolymerization (runs A, A_1, and A_2). Observed increase in the rates of AAm homopolymerization can be ascribed to the increase of AAm overall concentration (i.e., to the value of % AAm) in inverse microemulsion. Different sizes of inverse micelles in initial inverse microemulsions, regulated by the value of molar ratio [W]/[AOT][24] as well as of the ratio [T]/[AOT] do not influence the AAm polymerization rates. On the other hand, in the absence of AAm, e.g. in the case of BA homopolymerization in a toluene-based inverse microemulsion, the observed BA polymerization rate is very small. Thus, for example, the rate of BA homopolymerization is only 1/564 of the rate of AAm homopolymerization in the absence of BA (cf. Table 6, run A vs run B). For this is responsible the nature of the initiator used (APS is exclusively located in the dispersed water phase) and also the low solubility of BA in the dispersed water phase (0.14 mass %[25]). The rate

Table 6. Composition Parameters and Determined Maximum Polymerization Rates at a Given Monomer Conversion for Homopolymerization of Acrylamide (Runs A, A_1, A_2) and Butyl Acrylate (B, D, D_1) and Copolymerization of AAm/BA Couple (A_3, A_{31}, A_{32}, A_{33}, C) in Winsor IV (w/o) and Winsor I (o/w) Microemulsions T/BA/AOT/W/AAm/SDS/APS, Polymerization Temperature 60 °C

run[a]	[T]/[AOT]	[W]/[AOT]	AAm/W	BA/AAM	% AAm[b]	Φ_{aw}	R_p/au/% C
A	20.1	10.3	0.267	0.000	1.95	0.083	0.1128/17.34
A_1	20.1	20.6	0.267	0.000	3.57	0.153	0.1329/22.71
A_2	12.1	12.4	0.267	0.000	3.22	0.141	0.1239/21.19
A_3	11.6	6.2	0.267	1.250	1.63	0.076	0.0666/15.31
A_{31}	11.6	12.4	0.267	0.271	6.10	0.292	0.0264/32.70
A_{32}	11.6	46.5	0.267	0.172	8.08	0.387	0.0355/40.32
A_{33}	11.6	70.4	0.267	0.13	10.23	0.489	0.0335/25.74
B[c]	19.4	10.3	0.000		0.00	0.073	0.0002/2.33
C[d]	7.2	7.0	0.267	0.183	11.80	0.573	0.0244/28.73
D[e]	14.5	10.3	0.000		0.00	0.075	0.0151/28.02
D_1[f]	14.5	10.3	0.000		0.00	0.075	0.0012/10.70

[a] Volume fractions of aqueous phase, Φ_{aw}, in inverse microemulsions A_{31}, A_{32}, and A_{33} was changed by titration of inverse micro emulsion A_3 with water solution of AAm and SDS. SDS/ water = 0.000 (runs A, A_1, A_2) and 0.067 (runs A_3, A_{31}, A_{32}, A_{33}, B, C, D, D_1). Initiator: APS, 4.8×10^{-2} g per 100 g of dispersion system. [b] Mass %, related to the whole dispersion system. [c] Winsor IV monomer butyl acrylate containing (T/BA, 29/1 by mass) inverse microemulsion, no AAm present. [d] Titrated Winsor IV (A_3) inverse microemulsion by water solution of AAm and SDS to Φ_{aw} at which phase separation occurred and Winsor I o/w was formed (cf. Table 3). Data refer to lower microemulsion o/w phase. For polymerization of 100.00 mL of the lower microemulsion o/w phase (for composition see Table 5) initiator APS in an amount of 0.052 g was used. Attempts to polymerize traces of BA in the oil phase of inverse microemulsion were unsuccessful (see Results and Discussion and footnote *b* of Table 5). [e] Butyl acrylate instead of toluene was used as the oil phase. No AAm was present in the recipe.This case represents the APS initiated homopolymerization of BA in inverse microemulsion. The viscosity molecular weight of BA homopolymer was 2.23×10^5 g mol^{-1}. [f] See remark *e*. Here also no APS initiator was used. The case represents the thermal polymerization of BA in inverse microemulsion. The viscosity molecular weight of BA homopolymer was 3.12×10^5 g mol^{-1}.

of BA monomer radical formation (in comparison to the rate of formation of AAm monomer radical) is low and also low is the number of water phase exiting BA monomer radicals. Thus, the low initiation rate of BA polymerization is the main reason for the low values of BA polymerization rate in the oil phase. For (co)polymerization of the AAm/BA couple in inverse microemulsion, the fairly good solubility of AAm in the toluene oil phase (about 2 mass %[26]), as well as of BA in the water phase,[25] gives a good chance for both monomers to participate in the addition reactions with initiator and monomer radicals in the water and/or oil phase. Monomer radicals of AAm and of BA generated in the water phase may exit the water phase and enter in the addition reactions with BA and/or AAm in the oil phase. These water and oil phase processes lead to the formation of oligomer and (co)oligomer radicals and lately to homopolymers of AAm and/or BA and of (co)polymer of AAm and BA. The overall (co)polymerization rate in toluene-based inverse microemulsion containing AAm and BA (if BA/AAm $\neq 0$) depends on the values of the BA/AAm ratio in inverse microemulsion. The relatively small admixture of BA ($0 < \text{BA/AAm} = 0.271$) to the AAm-containing inverse microemulsion (runs A_{33}, A_{32}, and A_{31}) decreases the overall polymerization rate with respect to the rate of AAm homopolymerization until the minimum value (1/4.3) of the rate of polymerization (for BA/AAm = 0.271) was obtained. For the ratios of BA/AAM > 0.271, an increase of the overall polymerization rate was observed (run A_3).

It is interesting to note that the maximum (co)polymerization rate for AAm/BA couple in separated o/w microemulsion phase of Winsor I (run C, Table 6) is close (approximately $^2/_3$) to the maximum (co)polymerization rate for AAm/BA couple in w/o Winsor IV toluene-based inverse microemulsion (run A_{32}, Table 6). Both dispersion systems have practically the same value of BA/AAm ratio and identical AAm/W and SDS/W ratios. Although all other parameters differ significantly, their impact on the (co)polymerization rate obviously is not significant.Further studies are planned to illuminate this interesting problem in more details. Attempts to polymerize the supposed presence of traces of BA in the oil phase of Winsor I (o/w) inverse microemulsion were unsuccessful. No polymer was found after attempted polymerization initiation by dibenzoyl peroxide (0.25 g/100 mL of the oil phase).

It is worth mentioning that the maximum BA polymerization rate in thermally initiated (in the absence of APS) polymerization (run D_1,Table 6) is about $^1/_{10}$ of the maximum polymerization rate of APS-initiated BA homopolymerization. This relatively high rate and initiation mechanism of thermally initiated homopolymerization of BA is dificcult to explain. One can speculate that oxygen molecules present in the reaction system[27] copolymerize with BA monomer and/or function as radical traps. Because of scission of O−O bonds in the copolymer, only short chains are formed. Scission process generates alkoxy radicals which are trapped by oxygen molecules. Alkoxy radicals undergo also other reactions (e.g., addition, transfer, termination, etc.) in the reaction system. Addition reactions of alkoxy radicals with BA monomer lead to initiation of the BA polymerization. The determined viscosity molecular weight (footnotes *e* and *f* of Table 6) shows that in the inverse microemulsion system, a BA homopolymer of high molecular mass was formed. This also confirms the supposed formation of alkoxy radicals and their participation in addition reaction with BA monomer. Next, the formation of homopolymer of high molecular weight and the fact that monomer BA is not a very good solvent for BA homopolymer enlarge the impact of the gel effect on the rate of thermally initiated BA homopolymerization in inverse microemulsion.

Conclusions

It was shown that the titration of AAm/BA (co)monomer couple containing Winsor IV toluene-based inverse microemulsions ($\Phi_{aw} < 0.1$) by stepwise addition of water solution of AAm and SDS maintained a single-phase dispersion system in a broad region of volume fractions of aqueous phase, Φ_{aw},until the value of Φ_{aw2}, necessary for the formation of two-phase Winsor I dispersion system, was reached. The value of Φ_{aw2} depends on [T]/[AOT] and AOT/SDS of the initial Winsor IV inverse microemulsion. Titration of inverse microemulsion by water solution of AAm, water solution of SDS, or by water led to substantially lower values of Φ_{aw2} at which the transition Winsor IV → Winsor I occurred. During titration of the inverse microemulsion by water solution of acrylamide and SDS the composition of inverse microemulsion changes and the most important is the significant increase (up to 6-fold) of the AAm concentration in the dispersion system.

The (co)polymerization and homopolymerization rates of BA/AAm (co)monomer couple, AAm and/or BA monomer containing Winsor IV (W_TIV) toluene-based inverse microemulsions, Winsor IV ($W_{BA}IV$) butyl acrylate-based inverse microemulsion and microemulsion phase of Winsor I (W_TI) toluene-based dispersion system follow the sequence

$$\mathrm{AAm(W_TIV)} > \mathrm{BA/AAm(W_TIV)} \sim \mathrm{BA/AAm(W_TI)} > \mathrm{BA(W_{BA}IV)} > > \mathrm{BA(W_TIV)}$$

The kinetics of AAm/BA polymerization in Winsor IV w/o inverse microemulsion and in the microemulsion phase of Winsor I o/w microemulsion is predominantly influenced by the nature of free-radical initiator, solubility of initiator and monomers in the macro (continuous) phase and in the micro (dispersed) phase and concentration of initiator and monomers at the reaction locus.

It was also shown that for the mechanism of AAm/BA copolymer formation a significant role play the monomer radicals exiting the water phase and entering the oil phase. These monomer radicals start the radical reactions of the monomer(s) in the oil phase. As a result nanosized, partly hydrophobized (co)polymer particles are formed.

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References and Notes

(1) Barton, J. *Prog. Polym. Sci.* **1996**, *21*, 399−438.
(2) Candau, F.; Leong, Y. S.; Fitch, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **1985**, *23*, 193−214.
(3) Holtzcherer, C.; Durand, J.-P.; Candau, F. *Colloid Polym. Sci.* **1987**, *265*, 1067−1074.
(4) Barton, J. *Polym. Int.* **1993**, *30*, 151−156.
(5) Barton, J.; Tino, J.; Hlouskova, Z.; Stillhammerova, M. *Polym. Int.* **1994**, *34*, 89−96.
(6) Vaskova, V.; Juranicova, V.; Barton, J. *Makromol. Chem.* **1990**, *191*, 717−723.
(7) Barton, J. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 289−306.
(8) Barton, J.; Juranicova, V. *Macromol. Chem. Phys.* 1996, 197, 3177−3190.
(9) Barton, J.; Kawamoto, S.; Fujimoto, K.; Kawaguchi, H.; Capek, I. *Polym. Int.* **2000**, *49*, 358−366.
(10) Barton, J.; Juranicova, V. *Polym. Int.*, in press.
(11) Candau, F.; Collin, D.; Kern, F. *Makromol. Chem., Macromol. Symp.* **1990**, *35/36*105−119.
(12) Candau, F.; Zekhnini, Z.; Durand, J.-P. *J. Colloid Interface Sci.* **1986**, *114*, 398−408.
(13) Candau, F.; Buchert, P. *Colloids Surf.* **1990**, *48*, 107−122.
(14) Barton, J.; Stillhammerova, M.; Lezovic, M. *Angew. Makromol. Chem.* **1996**, *237*, 99−112.
(15) Winsor, P. A. *Trans. Faraday Soc.* **1948**, *44*, 376−386.
(16) Lezovic, M.; Ogino, K.; Sato, H.; Capek, I.; Barton, J. *Polym. Int.* **1998**, *46*, 269−274.
(17) Berger, K. C.; Meyerhoff, G. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; p II/67.
(18) Kurata, M.; Tsunashima, Y. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley and Sons: New York, 1989; p VII/8.
(19) Matsumoto, S. In *Macro- and Microemulsions: Theory and Applications*; Shah, D. O., Ed.; ACS Symposium Series 272, American Chemical Society: Washington, DC, 1985; p 415.
(20) Garti, N.; Aserin, A. *Adv. Colloid Interface Sci.* **1996**, *62*, 3799−3807.
(21) Barton, J.; Stillhammerova, M. *Angew. Makromol. Chem.* **1996**, *237*, 113−122.
(22) Eastoe, J. *Langmuir* **1992**, *8*, 1503−1506.
(23) Charvolin, J.; Sadoc, J. F. *J. Phys.* **1988**, *49*, 521−529.
(24) Pileni, M. P. In *Structure and Reactivity in Reverse Micelles*; Pileni, M. P., Ed.; Elsevier Science: Amsterdam, 1989; Vol. 65, p 44.
(25) Barton, J.; Capek, I. In *Radical Polymerization in Disperse Systems*, E. Horwood: Chichester, England, 1994; Chapter 3, p 140.
(26) Glukhikh, V.; Graillat, C.; Pichot, J. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 1127−1134.
(27) Short inhibition periods (few minutes) of polymerization in inverse microemulsions were always observed by us. They could not be eliminated by *vacuo/argon* purging method used for the creation of an inert atmosphere for polymerization.

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