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Inverse Microemulsion Polymerization of Acrylamide in the Presence of Bi-Unsaturated Vinyl Monomers

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The effect of divinylbenzene and *N,N*-methylenebisacrylamide on the polymerization of acrylamide in inverse microemulsion was studied. Studying the polymerization kinetics, polymer particle sizes, degree of swellability measurements, and the chemical composition of the products we have found that in the presence of bi-unsaturated vinyl monomers the character of conversion curve as well as crosslinking and particle sizes of the products have been changed. The interpretation of the obtained results is based on previously proposed mechanism of the initiation of free radical polymerization and formation and growth of polymer particles in inverse microemulsion.

Crosslinking of water-soluble vinyl monomers by bifunctional monomers in water has been studied in detail [1–4]. In these systems, deviations from the ideality have been observed. The gels prepared in this way have been considerably inhomogeneous and they contained domains of different degrees of crosslinking [3]. For the explanation of this phenomenon, several factors should be considered, e.g. various reactivity of double bonds in monomers [4], decreased reactivity of double bonds in polymers in comparison to that of their monomers, and the primary (inside of one molecule) and the secondary (between several molecules) cyclization [2]. A combination of all the above-mentioned factors could lead to a very high copolymerization rate, and at the same time, also to the appearance of macroscopic as well as microscopic inhomogeneities in the network of the gel obtained [1].

In the present work, we tried to utilize the possibilities provided by the usage of heterogeneous systems. One of them is also the copolymerization of comonomers of various water solubility. Therefore, the copolymerization of acrylamide with divinylbenzene and *N,N*-methylenebisacrylamide in inverse microemulsion has been studied from the viewpoint of the processes kinetics and of the basic characteristics of the products formed.

EXPERIMENTAL

Monomers acrylamide (AAM), pure (Fluka, Buchs, Switzerland) and *N,N*-methylenebisacrylamide (MBAAM), ultra pure (Polyscience, USA) have been used without further purification. Divinylbenzene (DVB) (Merck, Germany) has been deprived of in-

hibitor by sodium hydroxide solution and then distilled at reduced pressure in N_2 . The fraction boiling at about 50 °C was used for further polymerization. Emulsifier sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (Fluka) has been used without further purification. For experiments, toluene, anal. grade (Lachema, Czech Republic) and deionized water have been used. As radical initiators, dibenzoyl peroxide (DBP) (BHD Chemicals, England) and 2,2'-azobisisobutyronitrile (AIBN) (Fluka), both recrystallized from methanol, and/or ammonium peroxydisulfate (APS) (Lachema) without further purification, have been used. During the polymerization, an inert (argon) atmosphere has been maintained by bubbling through argon.

Procedures

The weighted amount of AAM and (in experiments with MBAAM) also of MBAAM, has been dissolved in 1.5–3 g of water. 3.6 g of AOT and (in experiments with DVB) also the appropriate amount of DVB have been dissolved in 15 g of toluene. The inverse microemulsion has been prepared by simple mixing of the oil and aqueous solutions. Through the transparent inverse microemulsion formed immediately, argon has been bubbled for 45 min. Then, 0.04 g of DBP, and/or 0.03 g of AIBN in a few drops of toluene, and/or 0.04 g of APS in a few drops of water have been added and argon has been bubbled through the reaction mixture for additional 5 min. The polymerization mixture prepared in this way has been filled into glass dilatometer consisting of a separable reaction vessel connected *via* a ground joint to the capillary. The filled dilatometer was put into a thermostat preheated to the temperature of 60 °C. After stabilization of the meniscus in the capillary,

the decrease of the meniscus has been measured by a cathetometer in chosen time intervals. When the changes of the meniscus in the capillary became inexpressive, polymer particle sizes of obtained final dispersions, d_T , have been measured by BI 90 Particle Sizer with an accuracy $\pm 3\%$.

To estimate the overall conversion gravimetrically, ca. 6 g of the final dispersion have been precipitated by technical ethanol. After at least tenfold decantation with ethanol, the precipitated polymers were dried to constant mass at 50 °C in vacuum.

Weighted amount of dry polymers has been swollen in 3 g of water. For "macro-crosslinked" samples that are insoluble in water, the parameter of swellability Q has been estimated as the ratio of water mass present in the sample at swelling equilibrium to the mass of dry sample.

In "micro-crosslinked" samples which are fully redispersible in water, polymer particle sizes of redispersed microgels, d_w , have been measured in water by BI 90 Particle Sizer. Composition of polymers prepared in the presence of DVB has been determined by elemental analysis by a WC Heraeus elemental analysis device.

RESULTS AND DISCUSSION

Polymerization of AAM in inverse microemulsion has been studied in detail using water- as well as oil-soluble initiators [5–8]. Results obtained by AAM polymerization kinetics study using DBP for initiation of inverse microemulsion polymerization, showed that the radicals formed during DBP decomposition in toluene could initiate the polymerization of even a very small amount of AAM dissolved in toluene [8]. Oligoradicals thus formed, after reaching their limit of solubility in toluene, precipitate and are captured

Table 1. Dependence of the Overall Conversion (α), the Nitrogen ($w(N)$) and AAM ($w(AAM)$) Content in the Polymer, the AAM ($\alpha(AAM)$) and DVB ($\alpha(DVB)$) Conversion, the Polymer Particle Sizes, d_T , and the Swellability of the Polymer Products in Water, Q , of the Final Dispersion, on the Reactants Amounts and Initiators Used, in the AAM Inverse Microemulsion Polymerization in the Presence of DVB

$m(H_2O)$ g	$m(AAM)$ g	$m(DVB)$ g	Initiator	α %	$w(N)$ %	$w(AAM)$ %	$\alpha(AAM)$ %	$\alpha(DVB)$ %	d_T nm	Q^a		
1.50	0.4	0.06	DBP	90	–	–	–	–	38	∞		
2.25	0.6	0.00	DBP	97	19.7	100	97	–	43	∞		
2.25	0.6	0.06	DBP	94	18.1	91.5	94.7	86.7	46	∞		
2.25	0.6	0.30	DBP	59	–	–	–	–	75	54		
2.25	0.6	0.60	DBP	45	16.8	85.3	76.8	13.3	135	16		
2.25	0.6	1.20	DBP	aggregates, not estimable							–	–
2.25	0.0	0.60	DBP	8	–	–	–	–	–	–		
3.00	0.8	0.08	DBP	–	–	–	–	–	75	–		
3.00	0.8	0.80	DBP	40	–	–	–	–	140	14		
2.25	0.6	0.60	AIBN	45	17.6	89.3	80.4	17.6	133	42		
2.25	0.6	0.60	APS	39	18.1	89.3	71.5	22.2	165	13		

^a $Q = m(\text{water})/m(\text{dry polymer})$ at swelling equilibrium at 25 °C. Reaction conditions: 60 °C, 15 g of toluene, amounts of initiators used: (DBP) 0.04 g, (AIBN) 0.03 g, (APS) 0.04 g.

by AOT micelles or form aggregates which are finally captured by the micelles. The oligoradicals could penetrate through the interphase between the water micropool and the oil macrophase into the AAM-rich region in the shell of the water micropool [8, 9]. Here, the propagation of the AAM polymerization (k_p being of the order of 10^4) takes place.

In the case when besides AAM, also oil-soluble DVB is present in the inverse microemulsion (results summarized in Table 1), one could imagine a similar course of reactions. Radicals formed during DBP decomposition can initiate the formation of oligoradicals of DVB molecules (almost all of them are in toluene macrophase), as well as of AAM molecules dissolved in toluene. DVB oligoradicals can undergo crosslinking which can lead to their decreased solubility in toluene. In this polymerization system, AAM as well as DVB oligoradicals are captured by micelles in the inverse microemulsion and act further as described above.

Results shown in Fig. 1 can support such a view of the processes in the investigated system. Here, overall conversion curves are shown for polymerization systems containing a constant amount of AAM and various amounts of DVB, using DBP for initiation. As can be seen, during the time of investigation we can follow the change of not only the total achieved conversion but also of the character of the conversion curves. Curve 1 illustrates a rapid polymerization process characteristic of inverse microemulsion polymerization of AAM [5]. Under addition of DVB, curves 2–5 take more and more

the character of a solution polymerization. Curve 6 illustrates the slow solution homopolymerization of DVB (with low monomer concentration). The conversions estimated at the end of experiments, correspond approximately to the total AAM conversion, but the more DVB is present in the systems, the longer are the times needed to reach these conversions. From the elemental analysis it is clear, too, that in the analyzed reaction products, mainly AAM units are present (Table 1). The polymer particle sizes determined in the final dispersion, are increasing with the increasing amount of DVB in the polymerization system (Table 1). If the DVB amount is twice the AAM amount in the investigated system (curve 5 in Fig. 1), insoluble aggregates are formed. This fact can support the idea of two competitive paths of reactions during the initiation by DBP in the inverse microemulsion containing AAM as well as DVB monomers. With increasing DVB concentration, the formation of crosslinked DVB oligoradicals becomes more and more evident. The degree of crosslinking of the products characterized by decreasing value of Q (Table 1) points out that at higher DVB content in the reaction mixture, the network becomes denser. At the same time, the rate of addition of DVB molecules either to the primary radical or to the growing oligoradical is different from the rate of addition of AAM molecules either to the primary radical or to the growing oligoradical. The overall course of the conversion curves has therefore to reflex also the probability of formation of the DVB units containing oligoradicals as a function of DVB

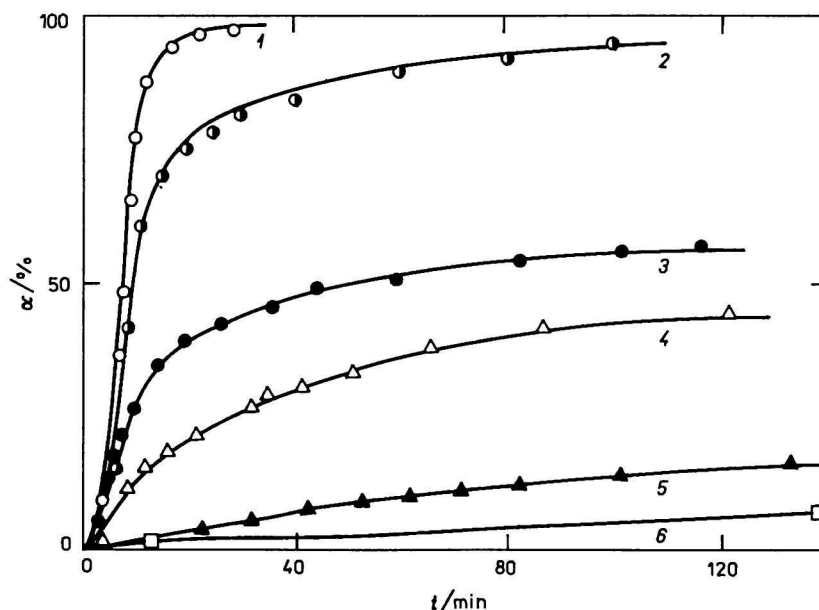


Fig. 1. Overall conversion curves of the acrylamide (AAM) inverse microemulsion polymerization in the presence of divinylbenzene (DVB) at 60 °C, initiated by dibenzoyl peroxide (DBP). Polymerization system: 15 g of toluene, 2.25 g of water, 3.6 g of AOT, 0.04 g of DBP. Except of the case illustrated by curve 6, 0.6 g of AAM was used. DVB amounts: 1. 0 g, 2. 0.06 g, 3. 0.30 g, 4. 0.60 g, 5. 1.20 g, 6. homopolymerization of 0.60 g of DVB.

concentration in the system. Another possibility to explain the increase of d_T with increasing DVB content can also be the swelling of possible present poly(DVB) in toluene.

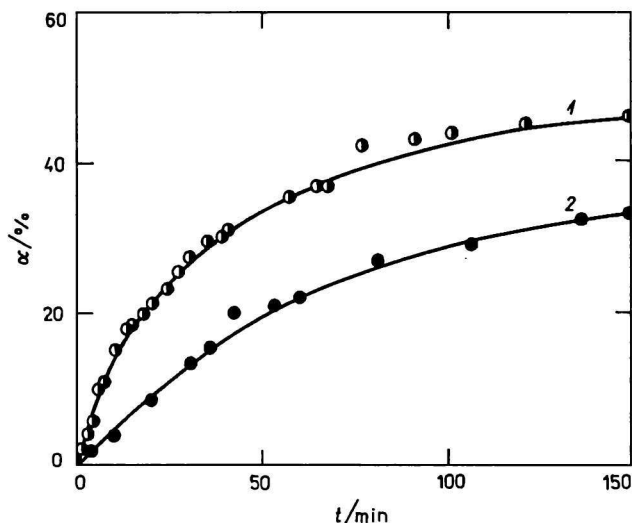


Fig. 2. Overall conversion curves of the acrylamide (AAM) inverse microemulsion polymerization in the presence of divinylbenzene (DVB) at 60 °C, initiated by dibenzoyl peroxide (DBP). Polymerization system: 15 g of toluene, 3.6 g of AOT, 0.04 g of DBP. 1. 2.25 g of water, 0.6 g of AAM, 0.6 g of DVB; 2. 3.0 g of water, 0.8 g of AAM, 0.8 g of DVB.

In Fig. 2, the polymerization curves of two various systems are illustrated. In these systems, the constant initiator DBP and emulsifier concentrations in 15 g of toluene have been used. In both systems the concentration of AAM in water as well as the mass ratio $m(\text{AAM}) : m(\text{DVB})$ are the same. They differ in the absolute amounts of water phases and therefore also in absolute amounts of DVB in the system. Curve 1 illustrates the overall polymerization curve in the system where less of water phase and, correspondingly, less of DVB has been taken into reaction. In this system, the polymerization proceeds more rapidly than in the system illustrated by the curve 2. Polymerization rates ($n/(V(\text{reaction system}) \cdot t)$) at 20% conversion (reached in the system 1 after 20 min of reaction, but in the system 2 after about 50 min of reaction) are following:

$$\begin{aligned} \text{For system 1 } R_p &= 6.8 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}; \\ \text{for system 2 } R_p &= 3.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}. \end{aligned}$$

The fact that despite of higher monomer concentration in the system 2 lower polymerization rate has been reached can be ascribed to the various rates of DVB- and AAM-oligoradicals formation (as described above). In the system 2, the slower rate of formation of crosslinked DVB oligoradicals is evident. In this system, final dispersion contains also larger polymer particles with denser network (lower values of Q).

The course of the AAM polymerization in inverse microemulsion in the presence of DVB illustrated in Fig. 3 shows that the more water there is in the system, the slower is the reaction (if all other concentration ratios are kept constant) (curves 1 and 2 in Fig. 3). The same is valid for the influence of AOT (curves 3 and 4 in Fig. 3). The influence of AOT can, however, be ascribed to degradative transfer reactions, typical for some anionic surfactants [10].

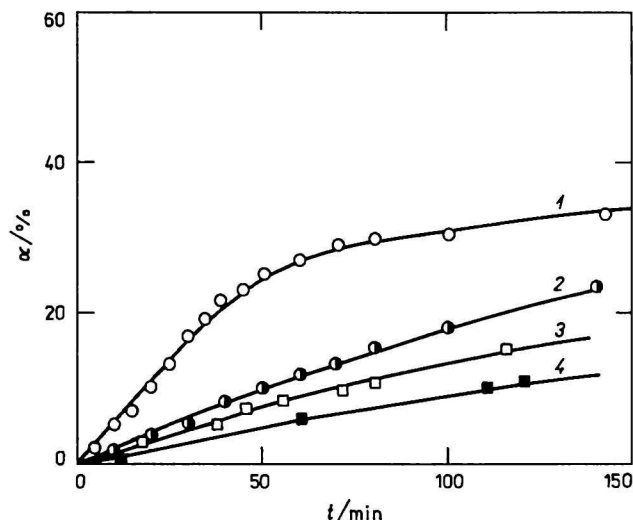


Fig. 3. Overall conversion curves of the acrylamide (AAM) inverse microemulsion polymerization in the presence of divinylbenzene (DVB) at 60 °C, initiated by dibenzoyl peroxide (DBP). Polymerization system: 15 g of toluene, 0.04 g of DBP. 1. 2.25 g of water, 1.2 g of AAM, 1.2 g of DVB, 3.6 g of AOT; 2. 4.5 g of water, 1.2 g of AAM, 1.2 g of DVB, 3.6 g of AOT; 3. 6.0 g of water, 1.6 g of AAM, 1.6 g of DVB, 5.4 g of AOT; 4. 6.0 g of water, 1.6 g of AAM, 1.6 g of DVB, 7.2 g of AOT.

Except for DBP, also partially water-soluble initiator AIBN and water-soluble initiator APS have been used for initiation of inverse microemulsion AAM polymerization in the presence of DVB. The overall conversion curves of systems containing the same amounts of all reaction components but differing in initiators used, are shown in Fig. 4. The rates of the polymerizations observed correspond to some extent to the values of decomposition constants of the initiators used [5]:

$$\begin{aligned} \text{For AIBN at 60 °C in toluene, } k_d &= 9.15 \times 10^{-6} \text{ s}^{-1}; \\ \text{for APS at 60 °C in water, } k_d &= 5.78 \times 10^{-6} \text{ s}^{-1}; \\ \text{for DBP at 60 °C in toluene, } k_d &= 2.83 \times 10^{-6} \text{ s}^{-1}. \end{aligned}$$

Consequently, the rates as well as the loci [6, 7] of initiation are decisive for the further polymerization reactions. As can be seen in Table 1, the crosslinking in the polymer particles formed in the final dispersions in the investigated systems also varies. In the AAM polymerization system, initiated by AIBN, the locus of initiation is proved to be mainly

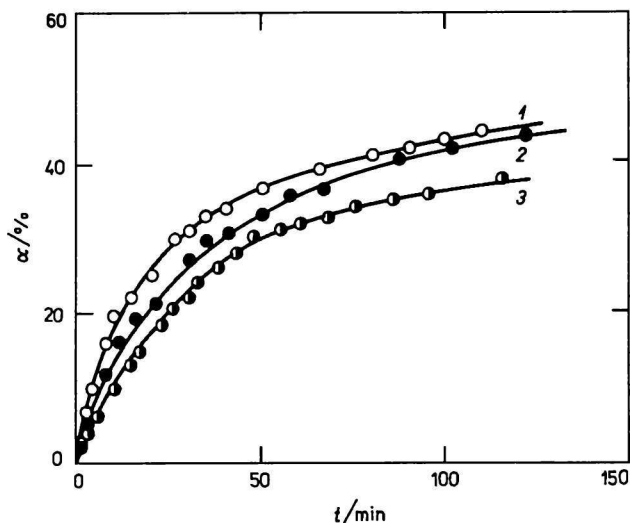


Fig. 4. Overall conversion curves of the acrylamide (AAM) inverse microemulsion polymerization in the presence of divinylbenzene (DVB) at 60 °C, initiated by various initiators. Polymerization system: 15 g of toluene, 2.25 g of water, 0.6 g of AAM, 0.6 g of DVB, 3.6 g of AOT. 1. Initiator AIBN (0.03 g); 2. initiator DBP (0.04 g); 3. initiator APS (0.04 g).

the interlayer between the water micropool and oil macrophase [6]. The radicals formed by AIBN decomposition in the interlayer are consumed during the reaction with AAM which is concentrated in the AAM-rich region of the water micropool in the shell close to the interphase [11]. During this polymerization, no dense network in the polymer particle could be formed. AIBN is dissolved also in toluene where it can initiate the formation of DVB radicals. This reaction may be responsible for a small number of crosslinks in the polymer particles.

In the case of initiation of the investigated system

by a water-soluble initiator APS, the decomposition of the initiator concentrated in the water micropool and the further course of the reaction might be influenced by the presence of AAM and of the anionic emulsifier in the locus of the initiation [6]. The acidity of the system might be increased due to the presence of the APS decomposition products, which, on the other hand, could enhance also imidization reactions of the amides leading to more crosslinked macromolecules (the smallest Q values in Table 1).

The polymerization of AAM in inverse microemulsion in the presence of DVB initiated by DBP has been described above. Besides DVB, also *N,N*-methylenebisacrylamide (MBAAM) has been used as a crosslinking agent of AAM polymerization in inverse microemulsion. 2.5, 5, and 10 mass % of the overall monomer amount has been taken into the copolymerization with AAM. The results obtained are listed in Tables 2 and 3, and shown in Fig. 5. To interpret these results, one has to take into account the differences found in AAM polymerizations in the so-called percolating and nonpercolating inverse microemulsions [12]. In the nonpercolating inverse microemulsion systems the micelles in the continuous oil phase are separated and the surface layers of the water micropools contain an AAM-rich region. In the percolating inverse microemulsions, water channels are formed, and so no AAM-rich region (as the main propagation locus) but an "averaged AAM concentration" is present. In nonpercolating systems, during the AAM polymerization initiated by DBP, a region of "slow" polymerization at low conversions can be observed. On the other hand, in the percolating systems such a "slow" polymerization region is very short. The rates of AAM polymerizations initiated by DBP beyond the "slow" polymerization re-

Table 2. Dependence of the Particle Sizes Measured in the Final Polymer Dispersion, d_T , and in the Redispersed Microgel in Water, d_W , Calculated Parameter of the Swellability of the Polymer Particles of the Redispersed Microgel in Water, Q' , and the Overall Conversion, α , on the Reactants Amounts in the AAM Inverse Microemulsion Polymerization in the Presence of MBAAM Initiated by APS

$m(\text{Monomers})$ g	$m(\text{H}_2\text{O})$ g	$w(\text{MBAAM})^a$ %	α %	d_T nm	d_W nm	Q'
0.4	1.5	0	95	31	—	—
0.4	1.5	5	95	30	55	34.6
0.4	1.5	5	99	30	57	37
0.4	1.5	10	50	30	61	99
0.4	1.5	10	69	27	67	120
0.4	1.5	10	100	21	53	85
0.8	3.0	0	67	52	—	—
0.8	3.0	0 ^b	100	45	—	—
0.8	3.0	5	95	48	70	15.5
0.8	3.0	5 ^b	80	40	65	26.2
0.8	3.0	10	100	74	89	7.8
0.8	3.0	10	99	72	86	7.5
0.8	3.0	10 ^b	81	67	91	14.8

a) Concentration of MBAAM represents 5 and/or 10 mass % of the overall amount of the monomers. b) Polymerized at 25 °C. Reaction conditions: 15 g of toluene, 3.6 g of AOT, 60 °C.

Table 3. Dependence of the Particle Sizes Measured in the Final Polymer Dispersion, d_T , and in the Redispersed Microgel in Water, d_W , Calculated Parameter of the Swellability of the Polymer Particles of the Redispersed Microgel in Water, Q' , and the Overall Conversion, α , on the Reactants Amounts in the AAM Inverse Microemulsion Polymerization in the Presence of MBAAM Initiated by DBP

$m(\text{Monomers})$	$m(\text{H}_2\text{O})$	$w(\text{MBAAM})$	α	d_T	d_W	Q'
g	g	%	%	nm	nm	
0.4	1.5	2.5	79	26	50	42.1
0.4	1.5	2.5	89	30	50	22.1
0.4	1.5	2.5	100	27	50	29.1
0.4	1.5	5.0	74	22	50	69.6
0.4	1.5	5.0	95	28	48	25.7
0.6	2.25	2.5	97	41	68	19.2
0.6	2.25	2.5	100	41	71	21.9
0.6	2.25	5.0	100	44	63	10.1

Concentration of MBAAM represents 2.5 and/or 5 mass % of the overall amount of the monomers. Reaction conditions: 15 g of toluene, 3.6 g of AOT, 60 °C.

gion are practically the same regardless of the inverse microemulsion nature (percolating or non-percolating) [12].

In Fig. 5, the conversion curves of AAM in a non-percolating (dotted line) and a percolating (dots □) systems are shown. The full dots illustrate the AAM polymerization in the presence of 5 mass % of MBAAM in a percolating (■) and nonpercolating (●) inverse microemulsion, respectively. Under addition of MBAAM, the region of "slow" polymerization can-

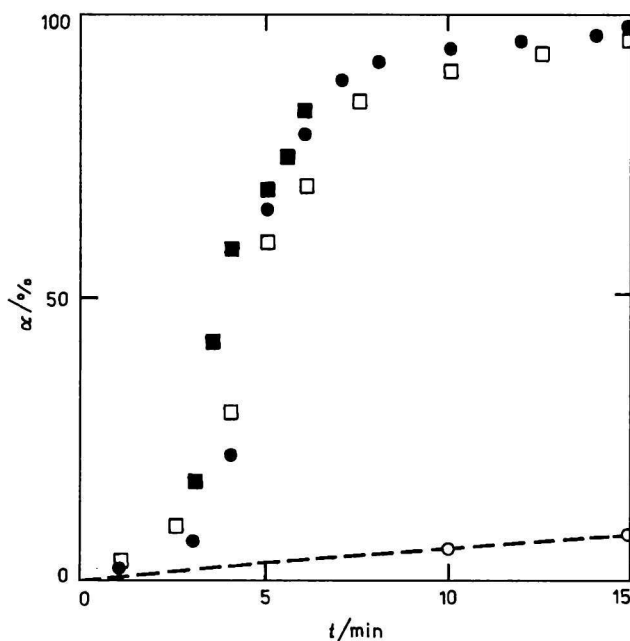


Fig. 5. Course of the polymerization of acrylamide (AAM) in the presence and/or absence of *N,N*-methylenebisacrylamide (MBAAM) in the percolating and non-percolating inverse microemulsion at 60 °C. Polymerization system: 15 g of toluene, 3.6 g of AOT, initiator 0.04 g of DBP. ○ 0.4 g of AAM, 1.5 g of water, without MBAAM; ● 0.38 g of AAM, 1.5 g of water, 0.02 g of MBAAM; □ 0.6 g of AAM, 2.25 g of water, without MBAAM; ■ 0.57 g of AAM, 2.25 g of water, 0.03 g of MBAAM.

not be observed. The course of the AAM polymerization in the presence of MBAAM in the percolating as well as nonpercolating inverse microemulsion is practically the same. Therefore it seems that even in the nonpercolating systems containing MBAAM, there is a possibility of forming the water channels with the less water-soluble monomers, facilitating the mass transfer between various phases of inverse microemulsion. In Tables 2 and 3, particle sizes of the final dispersions, d_T , the final total conversions, α %, as well as the particle sizes of the redispersed microgel in water, d_W , are summarized. Generally, the values of d_W were bigger than the sizes of the corresponding polymer particles in the final dispersion, d_T . This fact could point out that during the polymerization processes, in the systems containing MBAAM, crosslinks have been formed in these polymer particles.

We tried to calculate the "parameter of swellability" Q' in the reaction systems containing redispersible microgels, taking into account following considerations:

The number of polymer particles in the final dispersion, N , which is assumed not to change during the precipitation, drying, and redispersion of the polymer particles in water, could be calculated according to the relationship $N = V_s/v_p$, where V_s is the total redispersed phase volume (given as a sum of the water, monomer, and polar parts of the emulsifier volumes [5]). v_p is a polymer particle volume $v_p = d_T^3\pi/6$, where d_T is the experimentally obtained value of the polymer particle diameter in the final dispersion. The experimentally obtained particle diameter in the redispersed microgel, d_W , can be used for the calculation of the redispersed polymer particle volume $v_W = d_W^3\pi/6 = v_p + v_i$, where v_i is the volume of the water present inside every polymer particle of the redispersed microgel. Q' can be expressed by the relationship $Q' = m_i/m_p$, where m_i is the mass of v_i and m_p is the mass of dry polymer in every polymer particle in the redispersed microgel,

Table 4. Dependence of the Particle Sizes of Final Polymer Dispersions, d_T , and of the Calculated Parameter of the Swellability, Q' , on the Mole Ratio $x_r(w)$ between Water and AOT and on the Mole Ratio $x_r(m)$ between the Bifunctional Monomer and AAM in AAM Inverse Microemulsion Polymerization in the Presence and/or Absence of a Bifunctional Monomer, Initiated by DBP at 60 °C

Bifunctional monomer	$\frac{m(\text{AAM})}{\text{g}}$	$\frac{m(\text{H}_2\text{O})}{\text{g}}$	$x_r(w)^a$	$x_r(m)^b$	$\frac{d_T}{\text{nm}}$	Q'
–	0.40	1.50	10.3	0	37	–
0.01 g MBAAM	0.39	1.50	10.3	0.012	26	42.1
0.02 g MBAAM	0.38	1.50	10.3	0.024	28	25.7
0.04 g DVB	0.40	1.50	10.3	0.055	38	–
–	0.60	2.25	15.4	0	43	–
0.015 g MBAAM	0.58	2.25	15.4	0.012	41	19.2
0.03 g MBAAM	0.57	2.25	15.4	0.024	44	10.1
0.06 g DVB	0.60	2.25	15.4	0.055	46	–
–	0.80	3.00	20.6	0	52 ^c	–
0.04 g MBAAM	0.76	3.00	20.6	0.024	48 ^c	15.5
0.08 g MBAAM	0.72	3.00	20.6	0.051	74 ^c	7.8
0.08 g DVB	0.80	3.00	20.6	0.055	75	–

a) $x_r(w) = [\text{H}_2\text{O}]/[\text{AOT}]$; b) $x_r(m) = [\text{bifunctional monomer}]/[\text{AAM}]$; c) Initiated by APS. In every experiment 15 g of toluene is present.

$m_p = M/N$ (M is the total polymer mass in the final dispersion).

In Tables 2 and 3, the calculated values of Q are given. They are a function of the MBAAM percentage in the reaction systems, of the final dispersion conversions and/or of the total monomer amount in the reaction system.

A comparison of Q values in Table 1 with Q' values in Table 3 shows that under similar reaction conditions using the same initiator, swellability of the networks formed during the inverse microemulsion polymerization in the presence of either DVB or MBAAM is comparable. However, in the presence of DVB, "macro-crosslinked" polymer particles are formed, whereas in the presence of MBAAM obtained "micro-crosslinked" polymer particles could fully undergo redispersion in water.

In Table 4, polymer particle sizes, d_T , of the dispersions prepared by the AAM polymerization in inverse microemulsion in the presence of DVB and/or MBAAM are compared with those of the dispersions prepared by the AAM polymerization without any crosslinking agent in the same system.

From the data in Table 4 a conclusion can be drawn that polymer particle sizes, d_T , are not significantly influenced by the presence of bi-unsatu-

rated monomer in the comonomer mixture. The d_T values are mainly influenced by the original inverse microemulsion composition, i.e. by the water as well as acrylamide amount in the reaction mixture.

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