

Radical Emulsion Polymerization of *n*-Butyl Acrylate and Its Copolymerization with Acrylonitrile in the Presence of Crosslinker

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ABSTRACT: The batch emulsion polymerization of *n*-butyl acrylate (BA) and copolymerization of BA with acrylonitrile (AN) in the presence of divinylbenzene (DVB) or 1,6-hexamethylene diacrylate (HMDA) were investigated at 60°C using a water-soluble initiator. DVB was found to decrease both the rate of polymerization and particle size; this being more pronounced in homopolymerization systems. This is discussed in terms of the decrease of the monomer concentration in latex particles and transfer of radical activity from the particle interior to the particle surface or continuous phase. The entered radicals are supposed to be deactivated *via* the reaction with the residual vinyl groups of DVB in the particle interior. The hydrophilic AN monomer favored polymerization events in water and reduced the effect of DVB on the rate and particle size. The formation of the AN/BA copolymer enriched with BA was found to increase with DVB concentration. The DVB monomer favors the nucleation of micelles but suppresses kinetic events in the continuous phase. HMDA was found to be an inert crosslinking agent. This is ascribed to the formation of compact microgels due to the strong intramolecular crosslinking.

KEY WORDS Emulsion Polymerization / Rate of Polymerization / Polymer Particles / Copolymer Composition / Intra- and Intermolecular Crosslinking / Micellar Mechanism / Homogeneous Nucleation /

There are many studies on crosslinking reactions especially with DVB as a multifunctional crosslinking agent. These studies show that depending on the reaction conditions, different network structures are formed. In the case of a low concentration of a crosslinking monomer, a homogeneous network with statistical distribution of crosslinked joints are formed.¹ In the case of a high concentration of a crosslinking agent, intramolecularly crosslinked macromolecules (microgels) are formed.² It becomes apparent that in the presence of the divinyl compound polymerization deviates from an ideal kinetic model. This is result of the strong cyclization,

the formation of trapped radicals, and the compactness of the particle structures. Besides, the pendant vinyl groups take part in the polymerization process and lead to the formation of strongly internally crosslinked structures.³⁻⁵

We reported earlier⁶ the effect of the emulsifier concentration on emulsion polymerization of ethyl acrylate in the presence of DVB or HMDA. DVB was found to decrease both the rate of polymerization and polymer particle size. HMDA slightly increased the rate of polymerization as well as polymer particle size. In this paper, we studied the radical emulsion polymerization of BA and copo-

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lymerization of BA and AN to elucidate the effects of the water-solubility of unsaturated monomers, the monomer feed composition, and type and concentration of tetrafunctional monomer on polymerization behavior. The results are discussed in terms of crosslinking of polymer particles, compactness of microgels, reduced swelling of crosslinked polymer particles, transfer of radical activity from the interior to the surface of the particles, trapping of radicals in the unsaturated polymer network, formation of primary particles *via* nucleation of the monomer-swollen emulsifier micelles, and precipitation of oligomers from the continuous phase.

EXPERIMENTAL

Materials

Certified grade BA, AN, DVB (*ca.* 90% *p*-isomer, the rest *m*- and *o*-isomers) and HMDA monomers (from Merck) were used after purification by the usual method.⁵⁻⁸ The emulsifier sodium dodecyl sulfate (SDS, from Merck) and initiator ammonium peroxydisulfate (APS, from Lachema Brno, CSFR) were reagent grade and used directly without further purification. Twice-distilled water was used as a polymerization medium.

Polymerization Procedure

For measurements of conversion *versus* time data, the polymerizations were conducted at 60°C in a 250 ml three-necked glass reactor equipped with a teflon stirrer, a rubber septum and a balloon (filled up with nitrogen). The samples were taken out during polymerization and the reaction proceeded under nitrogen atmosphere. The agitation speed of all runs was adjusted at 400 rpm. The polymerization techniques used and polymer isolation from the latex are described in detail elsewhere.^{7,8} The conversions were determined by the gravimetric method. The polymerization rate was determined as the mean and maximum rate within the conversion range 30–60%. The

composition of copolymers was determined by C, H, N, (O) elementary analyses.

Particle-size determinations were made by light scattering method. The results are quoted as the effective particle diameter (D). The number of particles (N) was estimated from the experimental value of D , using eq 1⁹

$$N = (3 \cdot d_m \cdot m) / \{4 \cdot \pi \cdot d_p \cdot w \cdot (D/2)^3\} \quad (1)$$

where m/w is the weight ratio between monomer and water, d_m and d_p are densities of water and polymer, respectively.

The values of equilibrium monomer concentration in latex particles were determined by a "static swelling method" from the difference in the volume of the monomer-swollen and unswollen polymer particles and by measurements of particle growth.⁹ The swelling of nonpolymerizing latexes by BA monomer was performed by the simple procedure described elsewhere.^{8,10} Surface tension was measured on a Tensiometer K 10 (Kruss GmbH) at 25°C.

RESULTS AND DISCUSSION

Polymerization Rate

The conversion *versus* time data of the emulsion polymerization of BA initiated by a water soluble initiator APS in the presence of an anionic emulsifier SDS and a crosslinker DVB are presented in Figure 1. Conversion curves for the systems without or with the low DVB concentration showed a sigmoidal shape typical for the classical emulsion polymerization. The addition of higher amount of DVB ($[DVB] > 0.77 \text{ mol dm}^{-3}$) leads, however, to deviation from the emulsion polymerization kinetics; *i.e.*, the conversion curves take on a shape similar to that for the solution polymerization. Figure 1 and Table I show that the nucleation period increases with DVB concentrations. Generally, the length of the nucleation period is a function of emulsifier and initiator concentrations. The particle nucleation mostly ends with depletion of the

Table I. Variation of the kinetic parameters in the emulsion polymerization of BA with DVB concentration (Reaction mixture: 100 g of water, 66.6 g of BA, 0.0252 g of NaHCO₃, 2 g of SDS, 0.2 g of APS. Temp, 60°C)

[DVB] mol dm ⁻³	[DVB]/[BA]	$R_p \times 10^{3a}$ mol dm ⁻³ s ⁻¹	D^b nm	$N \times 10^{-17c}/1 \text{ dm}^3$	P_{cr}^d %	R_p/R_{p0}^e	N/N_0^f	d_p^g
0.00	—	19.0	111	1.0	5	1.0	1.0	1.15 ^h
0.25	0.05	2.5	73	3.7	15	0.13	3.7	3.4
0.51	0.1	1.3	61	5.6	20	0.067	5.6	6.2
0.77	0.15	0.5	48	12.0	—	0.026	12.0	13.3

^a The rate of polymerization was determined in the interval 2 as a maximum rate.

^b Final particle diameter.

^c Number of final particles per 1 dm³ water.

^d Critical conversion.

^e Ratio of rates with and without DVB.

^f Ratio of the number of particles with and without DVB.

^g Relative density of polymer estimated from $N = 1.0 \times 10^{17} \text{ mol dm}^{-3}$ (without DVB) and D (taken from Table I) using eq 1.

^h Reference 11.

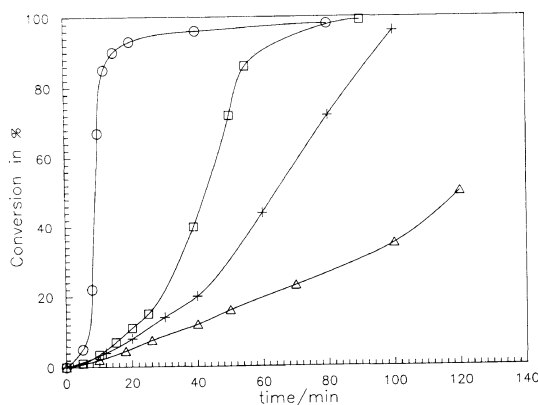


Figure 1. Variation of monomer conversion in the emulsion polymerization of butyl acrylate (BA) with the reaction time and DVB concentration. Reaction mixture: 100 g of water, 66.6 g of BA, 0.0252 g of NaHCO₃, 2 g of sodium dodecyl sulfate (SDS), 0.2 g of ammonium peroxodisulfate (APS). Temp, 60°C. [DVB]/(mol dm⁻³) = 0 (○); 0.25 (□); 0.51 (+); 0.77 (△).

micelles or free-emulsifier molecules. The formation of new primary particles ceases at time t or a critical conversion P_{cr} , when there is no free emulsifier to stabilize them and mostly ends at conversions below 5%.⁹ In the present study, all experiments were carried out at the same concentration of emulsifier and therefore, shift in the critical conversion can not be

ascribed to any changes in the emulsifier concentrations.

The micellar mechanism is generally applied to monomers with a sparing water-solubility, such as BA. The water-solubility of BA and DVB is 11 mM⁹ and 0.5 mM (estimated from data listed in,¹²⁻¹⁴ respectively. The addition of monomer units to the primary radicals is required to favor the entry of radicals to particles and the precipitation of oligomers from the aqueous phase.¹⁵

The initiation in the aqueous phase is accepted also for sparingly water-soluble monomers such as BA or styrene.^{12,14} The number-average degree of polymerization of BA or DVB oligomers (m) which separate from the aqueous phase can be estimated using the following equation

$$P_{n,m} = \frac{R_p}{R_i} = \frac{k_p}{k_t^{0.5}} \frac{[M]_{aq}}{R_i^{0.5}} = k_p \cdot [M]_{aq} \left[\frac{[I]}{(2fk_d k_t)} \right]^{0.5} \quad (2)$$

where R_p is the rate of polymerization, R_i the rate of initiation, k_p the rate constant for propagation, k_t the rate constant of termination, f the initiator efficiency, k_d the initiator decomposition rate constant and $[M]_{aq}$ the

Table II. Variation of the kinetic parameters in the emulsion copolymerization of BA and AN with DVB concentration (Reaction mixture: 100 g of water, 33.3 g of BA, 33.3 g of AN, 0.0252 g of NaHCO₃, 2 g of SDS, 0.2 g of APS. Temp, 60°C)

[DVB]	[DVB]/[BA]	$R_p \times 10^3$ ^a	D ^b	$N \times 10^{-17c}/1 \text{ dm}^3$	P_{cr} ^d	R_p/R_{p0} ^e	N/N_0 ^f
mol dm ⁻³		mol dm ⁻³ s ⁻¹	nm		%		
0.00	—	5.3	103	1.0	10	1.0	1.0
0.13	0.05	4.3	80	2.1	15	0.81	1.8
0.25	0.1	4.0	75	2.9	15	0.75	2.9
0.51	0.2	2.7	70	3.6	20	0.51	3.6
0.77	0.3	1.9	68	4.1	20	0.36	4.1

^{a-f} cf., Table I.

amount of monomer dissolved in the aqueous phase. The degrees of polymerization of the BA and DVB oligomers, $P_{n,m}$, calculated according to eq 2 using $k_p(\text{BA}) = 0.68 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_t(\text{BA}) = 6.4 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $[\text{BA}]_{\text{aq}} = 11.0 \times 10^{-3} \text{ mol dm}^{-3}$, $k(\text{St}) = 200 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_t(\text{St}) = 6.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $[\text{DVB}]_{\text{aq}} = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$, $f = 0.5$, $k_d = 5.7 \times 10^{-6} \text{ s}$ for peroxodisulfate and $[\text{APS}] = 8.76 \times 10^{-3} \text{ mol dm}^{-3}$ at 60°C^{16,17} were ca. 13 and < 1 , respectively. The values of $P_{n,m}$ were calculated assuming that propagating radicals of BA and DVB terminate by combination. The most important conclusion of these simple calculations is that the polymerization of BA or the growth of BA oligomer radicals proceeds in the continuous phase, whereas that of DVB is suppressed. In support of the calculation are the results of the emulsion polymerization of a very low water-soluble *p*-tert-butylstyrene (ca. 0.2 mM¹⁸). The *p*-tert-butyl styrene monomer does not polymerize in water but polymerizes in the presence of emulsifier micelles. Thus, the DVB monomer is expected to influence kinetic events in the monomer-swollen micelles and monomer droplets.

Table I shows that rate depression in the interval 2 (the medium conversion range) increases with DVB concentration.

Figure 2 shows the results of the emulsion copolymerization of the hydrophobic BA and

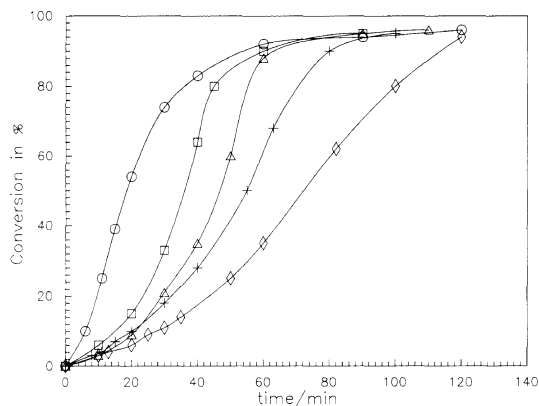


Figure 2. Variation of monomer conversion in the emulsion copolymerization of BA and acrylonitrile (AN) with the reaction time and DVB concentration. Reaction mixture: 100 g of water, 66.6 g of BA, 0.0252 g of NaHCO₃, 2 g of SDS, 0.2 g of APS. Temp, 60°C. $[\text{DVB}]/(\text{mol dm}^{-3}) = 0$ (○); 0.13 (□); 0.25 (△); 0.51 (+); 0.77 (◇).

hydrophilic AN and effect of DVB concentration initially charged on the monomer conversion *versus* time data. All conversion curves showed the sigmoidal shape.

Figure 2 and Table II show that the nucleation period increases with DVB concentration. The rate of polymerization decreases with increasing DVB concentration. This decrease in rate is smaller compared to that observed in the BA/DVB system. The polymerization of high-water soluble AN (~7 g/100 g water) favors polymerization in water and the formation of particles by

Table III. Variation of the kinetic parameters in the emulsion copolymerization of BA and AN with HMDA concentration (Reaction mixture: 100 g of water, 33.3 g of BA, 33.3 g of AN, 0.0252 g of NaHCO₃, 2 g of SDS, 0.2 g of APS. Temp, 60°C)

[HMDA] mol dm ⁻³	[HMDA]/[BA]	$R_p \times 10^3$ ^a mol dm ⁻³ s ⁻¹	D^b nm	$N \times 10^{-17}$ ^c /l dm ³	P_{cr} ^d %	Coag. ^e wt%
0.00	—	5.3	103	1.0	10	5.1
0.15	0.06	3.3	103	1.0	10	0.4
0.29	0.11	3.8	100	1.1	10	0.9
0.44	0.17	5.0	100	1.1	5	1.4

^{a-d} *cf.*, Table I.

^e Amount of coagulum at the end of polymerization per 100 g of monomer.

homogeneous nucleation.¹⁹ The increase of the AN fraction in the monomer feed increases the nucleation period and depresses the overall rate of polymerization due to the formation of less stable particles and their coalescence. Thus, the polymerization in water, homogeneous nucleation, and growth of particles seem to depress the crosslinking effect of DVB. The high water solubility of AN favors the desorption of radicals from the crosslinked polymer particles which can kinetically dominate the polymerization process. Thus, transfer radical activity from polymer network to monomer and by the exit to the continuous phase may decrease the fraction of trapped radicals. In the emulsion polymerization of hydrophilic monomers such as methyl methacrylate²⁰ and ethyl acrylate²¹ the desorption of radicals from the non-crosslinked polymer particles decreases the average number of radicals per particle (n) and rate of polymerization.

HMDA was found to be an inert crosslinking agent; it did not influence the rate of polymerization (Figure 3, Table III). Thus, swelling as well as kinetic events are not influenced by the HMDA crosslinker.

The average fractional rate per particle $R_p/([BA]_{aq} \cdot N)$ (using R_p and the monomer concentration for the interval 2 and final number of particles) may be taken as a semiquantitative equivalent of n (the average number of non-trapped radicals per particle)

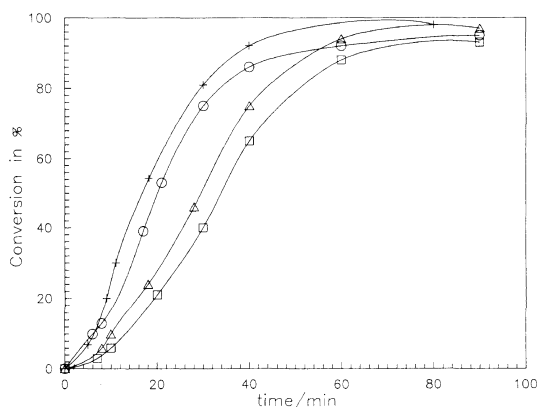


Figure 3. Variation of monomer conversion in the emulsion copolymerization of BA and AN with the reaction time and 1,6-hexamethylene diacrylate (HMDA) concentration. Reaction mixture: 100 g of water, 66.6 g of BA, 0.0252 g of NaHCO₃, 2 g of SDS, 0.2 g of AP. Temp, 60°C. [HMDA]/(mol dm⁻³) = 0 (○); 0.15 (□); 0.29 (△); 0.44 (+).

while k_p is constant in interval 2. The data in Tables IV and V show that $R_p/([BA]_{eq} \cdot N)$ (and thus n) strongly decreases by the addition of a small amount of DVB. The decrease is more pronounced in the BA/DVB system. If we suppose that the number of particles is independent of crosslinker concentration (see later) and decrease in the particle size is caused by crosslinking (more compact particles are formed) decrease in n with [DVB] should also be observed (see Table IV, column b). This indicates that the crosslinking decreases the

Table IV. Properties of final polyBA latexes

[DVB] mol dm ⁻³	[BA] ^a mol dm ⁻³		$R_p/([BA]_{eq} \cdot N) \times 10^{21}$ ^b s ⁻¹		γ^c mN m ⁻¹	$[\zeta]^d$ cm ³ g ⁻¹	Coag. ^e wt%
	I	II	I	II			
0.0	3.8	3.9	50.0	50.0	47.5	4.5	0.2
0.25	2.4	—	2.8	10.4	54.0	0.67	0.1
0.51	0.8	0.5	2.8	16.2	55.0	0.35	0.0
0.77	0.4	0.5	1.0	12.5	57.5	0.17	0.0

^a Equilibrium monomer concentration in the latex particles. I. Calculated from the dependence of the particle size *versus* the conversion. II. Obtained by the static swelling method.

^b Average fractional rate per particle. I. Using (different) N values from Table I. II. Using (same) $N = 1.0 \times 10^{17}$ particles · dm⁻³.

^c Surface tension.

^d Intrinsic viscosity.

^e *cf.*, Table III.

radical activity of particles.

The free vinyl groups in the polymer network were reported to react with the small-mobile radicalic reagents.²² These results²² indicate that the diffusion of radicals throughout the crosslinked particle interior leads to deactivation of the radical activity due to: 1) reactions of radicals with the pendant vinyl groups trapped in network and 2) the addition of monomer units to radicals. The reaction of radicals with the pendant vinyl groups leads to the formation of trapped radicals. The increase of the molecular weight of active polymer chains decreases their mobility. This results from the finding²³ that the increased crosslink density and size of reagents impede the rate of transport of species (radicals) through the polymer network.

The trapping of entered radicals is expected to proceed *via* the reaction with pendant vinyl groups which can be described as a first-order radical loss process. The particle interior thus seems to act as a trapping cage in which radicals can enter but can not exit.

The high hydrophilicity of HMDA (the water-solubility *ca.* 50 mM, estimated from data listed in¹²) or its acrylic groups and structural features of HMDA are supposed to

be responsible for the low crosslinking efficiency of this crosslinker. The hydrophilic microgels formed during the polymerization are supposed to separate from the hydrophobic reaction medium and form new microphase with high concentrations of acrylic groups.²⁴ This is expected to depress the intermolecular crosslinking reactions and increase intramolecular propagation events. The structural features of HMDA (two acrylic groups are separated by the long alkyl group) are expected to favor, at every intramolecular propagation step, the reactions of radicals with pendant unsaturated groups on their own chains or microgels (due to easy rotational motion of chain segments and the elastic network chain).²⁵ Thus, these phenomena should transfer the tetrafunctional HMDA (or a polymer chain carrying a radical and an unsaturated group) to a bifunctional (or the growing radical) monomer.

Particle Size

Variation of the particle size, D , with conversion for three different systems (without or with the crosslinking agent) is illustrated in Figures 4–6. In the emulsion polymerization of butyl acrylate, particle size increases up to 40 or 50% conversion and then levels off. The

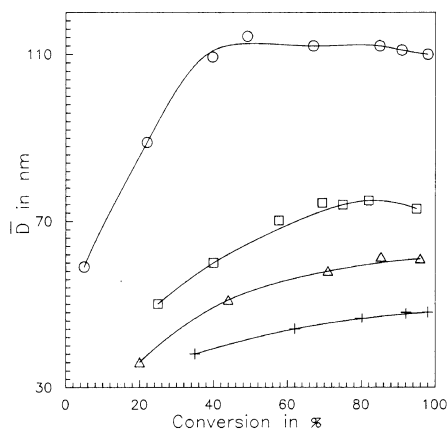


Figure 4. Variation of the average particle diameter, D , in the emulsion polymerization of BA with conversion and DVB concentration. $[DVB]/(\text{mol dm}^{-3})=0$ (○); 0.25 (□); 0.51 (△); 0.77 (+). Other conditions as given in the legend to Figure 1.

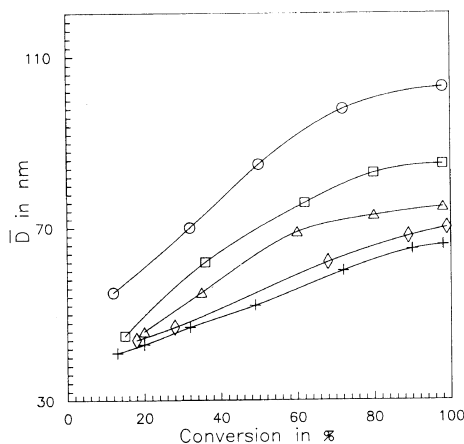


Figure 5. Variation of the average particle diameter, D , in the emulsion copolymerization of BA and AN with conversion and DVB concentration. $[DVB]/(\text{mol dm}^{-3})=0$ (○); 0.13 (□); 0.25 (△); 0.51 (◇); 0.77 (+). Other conditions as given in the legend to Figure 2.

most intensive increase in particle size is observed at low conversions. In this region the growth of particles may proceed also by association of small unstable particles.²⁶ After the depletion of monomer droplets (*ca.* at 40 or 50% conversion) particle size is constant or slightly decrease with conversion. The decrease in particle size is ascribed to the shrinkage of

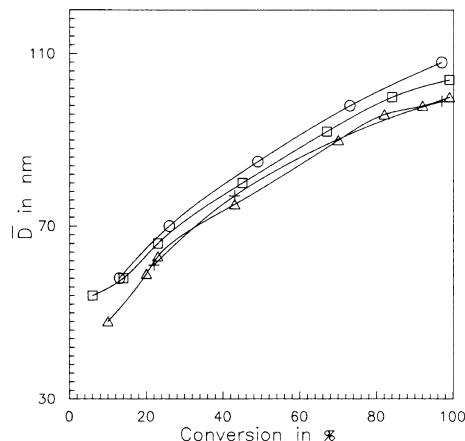


Figure 6. Variation of the average particle diameter, D , in the emulsion copolymerization of BA and AN with conversion and HMDA concentration. $[HMDA]/(\text{mol dm}^{-3})=0$ (○); 0.15 (□); 0.29 (△); 0.44 (+). Other conditions as given in the legend to Figure 3.

the monomer-swollen polymer phase. The addition of DVB changes the shape of particle size *versus* conversion curve and also decreases average particle size. DVB depresses the growth of polymer particles over the whole range of conversion and shifts the point at which particles end their growth to higher conversion. The end of particle growth is generally connected with the depletion of monomer droplets. Thus, increase in the number of crosslinks in particles decreases the swelling of polymer particles and equilibrium monomer concentration in the particles (Tables IV and V).²⁷⁻²⁹ The decrease of the monomer fraction in the monomer-swollen polymer particles results in increase of the monomer amount in monomer droplets and shift of the end of the interval 2 to higher conversion. Generally, the transition between intervals 2 and 3 indicates the depletion of monomer droplets and represents the weight ratio of monomer/polymer $w_{m/p}$ and/or equilibrium monomer concentration $[M]_{eq}$ in the particles.⁹ The equilibrium monomer concentrations $[BA]_{eq}$ calculated from the dependence of particle size *versus* conversion and end of particle growth (see Figure 4) are summarized

Table V. Properties of final poly(BA-co-AN) latexes

[DVB] mol dm ⁻³	$\frac{[\text{BA}]_{\text{eq}}^{\text{a}}}{\text{mol dm}^{-3}}$ I	$R_{\text{p}}/([\text{BA}]_{\text{eq}} \cdot N) \times 10^{21\text{b}}$ s ⁻¹	γ^{c} mN m ⁻¹	$[\zeta]^{\text{d}}$ cm ³ g ⁻¹	Coag. ^e wt%
0.0	3.5	15.0	48.0	2.5	5.1
0.13	2.9	8.2	50.0	2.1	2.0
0.25	1.4	9.8	50.5	1.8	1.5
0.51	1.4	5.3	53.9	1.4	1.1
0.77	0.7	6.5	54.7	1.2	0.8

^{a-c} *cf.*, Table II.

in Table IV (the column a). They agree well with those obtained in separate experiments by the static swelling method (Table IV, column b).

Table I shows that the number of particles increases with DVB concentration. From the experimental results the following expression can be derived

$$N \propto [\text{DVB}]^{4.5} \quad (3)$$

Equation 3 shows that the number of particles is proportional to the 4.5 order of DVB concentration which seems very high. Generally, the number of particles is independent of monomer concentration.⁹ From the foregoing discussion it appears that 4.5 results not only from increased particle nucleation but also from crosslinking reactions. Crosslinking generates smaller and more compact particles. In the case when N is independent of [DVB] eq 1 can be used to estimate the density of polymer network. The estimated values of polymer density show that the compactness of particles increases with [DVB] (Table I). The real values of polymer density are expected to be located between these two cases, *i.e.*, $N \propto [\text{DVB}]^{4.5}$ ($d_{\text{p}} = 1.2$) and $N \propto [\text{DVB}]^0$ ($d_{\text{p}} > 1.2$).

In the emulsion copolymerization of AN and BA, polymer particles were found to grow to high conversion with or without DVB (Figure 5). A high water-solubility of AN and precipitation of AN oligomers from the

continuous phase have been reported responsible for the growth of particles during polymerization.^{19,30} The polymerization of AN in water generates oligomers radicals and colloidal unstable primary particles which associate with themselves or/and with large polymer particles. In the BA/AN/DVB system the number of particles is proportional to 1.5 of the DVB concentration. This indicates that particle growth by association mechanism depresses crosslinking. The equilibrium monomer concentrations for the systems with AN are higher. The incompatibility of polyAN or copolymer rich in AN with the polymer matrix may play also some role in the polymerization mechanism.

The tetrafunctional monomer HMDA does not influence the size and number of particles but depresses slightly the formation of coagulum.

The crosslinking is known to proceed from the beginning of polymerization of multifunctional monomer.³¹ Crosslinked primary particles are formed *via* the polymerization of monomer in the aqueous phase (mainly for AN) and nucleation of the monomer-swollen (BA and DVB) emulsifier micelles. In the early stage of polymerization, predominant intramolecular crosslinking takes place and results in the formation of crosslinked primary particles due to the presence of pendant vinyl groups in the oligomers or primary (or small)

particles.^{5,32} The major characteristics of crosslinked primary particles is the low radical activity due to the hindered mobility of radicals and vinyl groups and low equilibrium monomer concentration. The low monomer concentration negatively influences propagation steps and particle growth. The slow growth of crosslinked particles may favor the nucleation of larger number of monomer-swollen micelles due to the slow consumption rate of free emulsifier molecules. The formation of polymer network favors the transfer of the polymerization loci from the particle interior to the continuous phase and/or particle shell (contribution of the solution polymerization³³).

Polymer and Latex Properties

The intrinsic viscosity of the soluble fraction of polymer was found to decrease with increasing concentration of DVB in the system (Tables IV and V). This agrees with Batzilla and Funke²⁹ on solution copolymerization. They reported that this behavior corresponds to change from linear to intra- and intermolecular crosslinked macromolecules. In the early stage of crosslinking (the solution polymerization), predominant intramolecular crosslinking results in the formation of reactive microgels (intramolecularly crosslinked growing chain), but as the reaction proceeds these microgels are crosslinked intermolecularly by reactions between vinyl pendant groups and radicals at the surface of different microgels, and microgels are transported to macrogels (the gel point³⁴). Intramolecular crosslink formation increases linearly with increasing pendant vinyl groups in the polymer and with the extent of reaction and depends on the structural characters of microgels. Shrinkage of microgel molecules due to intramolecular crosslinks (cyclizations) taking place during the polymerization is supposed to be responsible for the decrease of intrinsic viscosity. The intermolecular crosslink formation, in contrast, decreases with the extent of the reaction, because the increase in intramolecular cross-

links prevents interpenetration of polymer coils. It also decreases with the molecular weight of microgels and viscosity of the reaction media but is responsible for the growth of polymer coils or microgels.

In the emulsion system, however, from the beginning the polymerization proceeds in monomer-swollen polymer particles under high conversion conditions. The constant concentration of monomer in particles is kept by the diffusion of monomer from the monomer droplets through the aqueous phase. Primary radical termination, chain transfer processes and desorption and re-exit of radicals are important in the whole polymerization mechanism. Under these conditions, crosslinking reactions taking place in particles should differ from those in solution polymerization. For example, the weight ratio of monomer to polymer for polyBA particles swollen by BA is *ca.* 1.5. Thus, the polymerization proceeds under the conditions of 40 or 50% conversion at which bimolecular termination between growing radicals is already suppressed. In the presence of DVB, the weight ratio of monomer to polymer is much less. Thus, polymerization proceeds at around 60% or higher conversion. This means, that bimolecular termination or propagation reactions between microgels are suppressed. Under such conditions, polymerization in particles should be governed mainly by the intramolecular termination or propagation. Both should lead to decrease of the radical activity of polymer particles. The rate of polymerization was found to decrease with DVB concentration. However, the network formation is achieved by intermolecular crosslinking among different microgels. This probably takes place at high conversion after depletion of monomer droplets.

Crosslinking reactions are also a function of the nature of a crosslinking agent. Hydrophobic DVB molecules or microgels can easily penetrate into the hydrophobic particle core and there participate in crosslinking reactions. A hydrophobic medium, however, can act as

a poor solvent for the hydrophilic HMDA crosslinker. The conformation of microgels in poor solvents is known to change to a very compact one. Thus, the large fraction of the pendant vinyl groups inside such HMDA microgels may fail to undergo further reactions.³⁵

The formation of coagulum was found to decrease with increasing the DVB concentration (Tables IV—VI). This behavior results from the increase of both the surface area of particles and polymer fraction in particles which increase the fraction of emulsifier adsorbed on the particle surface.³⁶ The surface tension was found to increase with increasing the surface area of particles.

Copolymer Composition

Variation of the experimental cumulative average copolymer composition, F_{AN} , for two different systems (with and without DVB) with conversion and the DVB concentration is illustrated in Figure 7. The predicted copolymer composition data and monomer feed parameters are summarized in Table VI. The copolymer composition-conversion dependence in the absence of the crosslinking agent shows a monotoneous character. In the presence of DVB enrichment of the copolymer in BA units in the range of low conversion is observed. These results indicate that DVB suppresses the polymerization of AN and favors the polymerization of BA. The copolymerization of BA and AN was reported to produce the copolymer enriched with acrylonitrile at very low conversion.¹⁸ This is ascribed to the polymerization of AN in water, precipitation of oligomeric species and formation of primary particles rich in AN structural units. The transfer of DVB to the aqueous phase by AN seems to lead to retardation of aqueous phase kinetic events (the depressed growth of oligomer radicals). The copolymer enriched in BA results also from the monomer distribution history in the system. Hydrophobic BA is mainly located in

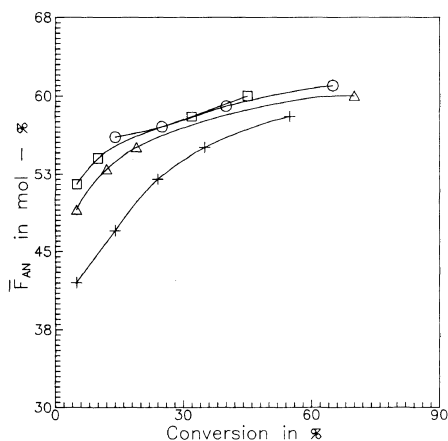


Figure 7. Variation of the cumulative copolymer composition, F_{AN} , with conversion for various DVB concentrations. $[DVB]/(\text{mol dm}^{-3}) = 0$ (○); 0.25 (□); 0.51 (△); 0.77 (+). Other conditions as given in the legend to Figure 1.

Table VI. Monomer feed and copolymer composition data

$[AN]^a$	$[BA]^a$	$[DVB]^a$	F_{AN}^b
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol%
6.3	2.6	0.0	70
6.3	2.6	0.25	66
6.3	2.6	0.51	62
6.3	2.6	0.77	60

^a Initial monomer concentration.

^b Instantaneous copolymer composition predicted from the single composition equation³⁷ and literature reactivity ratios ($r_{AN} = 1.08$ and $r_{BA} = 0.816^{38}$) using initial monomer concentrations.

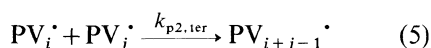
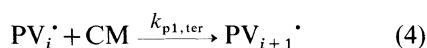
the monomer droplets and micelles and AN also in water. Under such conditions the polymerization in the micelles can lead to the formation of a copolymer more rich in BA units. The copolymerization data indicate that DVB suppressed the homogeneous nucleation of particles but favors the polymerization in micelles. The latter may result from the high radical trapping activity of the DVB network which depresses the high exit rate of radicals from the micelles and/or primary particles.²⁶

CONCLUSIONS

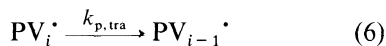
From the foregoing discussion it appears that the tetrafunctional DVB monomer suppresses growth events due to the decrease of monomer concentration in compact particles. The reduced rate of polymerization may lead to the nucleation of a larger number of monomer-swollen micelles. The crosslinked polymer particles are supposed to act as a radical trapper, *i.e.*, the entered radicals lose their activity by the first-order processes. Structural and hydrophobic properties of a crosslinker are supposed to be important in the whole polymerization and crosslinking mechanism. The high intramolecular propagation efficiency is supposed to be responsible for the deactivation of HMDA crosslinker. In the AN systems the DVB monomer favors the formation of particles by the micellar mechanism but suppresses the homogeneous nucleation events.

A possible mechanism for the reaction of reactive microgels (intramolecularly cross-linked growing chains) in the monomer swollen polymer particles is:

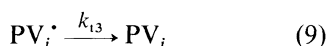
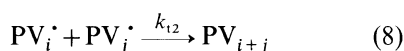
intermolecular propagation



intramolecular propagation



termination



where CM is a crosslinker, PV_i^{\cdot} and PV_j^{\cdot} are reactive microgels with *i* and *j* pendant vinyl groups, PV_i and PV_j inactive microgels, R a primary radical derived from the initiator by its decomposition, $k_{p1,ter}$ and $k_{p2,ter}$ the rate constant of intermolecular propagation and k_{t1} , k_{t2} and k_{t3} rate constants of primary-growing radical, growing-growing radical and monomolecular radical loss reactions.

Intermolecular propagations characterized by eq 4 and 5 are responsible for the growth of polymer chains or microgels. The former increases the size of microgels whereas the latter transforms the microgels into macrogels. The high viscosity of reaction media favors the diffusion of the low molecular weight monomer and its propagation on the surface or within the microgels. In favor of this assumption is the mode of transfer of monomer in the emulsion system. The close packing of microgels may initiate the gelation of particles but mainly after depletion of monomer droplets. The high polymer fraction in particles decreases the thermodynamic quality of reaction media which also favors the intramolecular propagation reactions (eq 6).

The high mobility of primary and oligomer radicals is supposed to be very effective in deactivation processes in particles (eq 7). The probability of deactivation of active microgels in bimolecular processes is very low (eq 8). This reaction is limited by mobility of microgels. The formation of compact microgels or macrogels should favor the deactivation of radical activity due to the formation of occluded or trapped radicals (eq 9).

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