Colloid Polym Sci (2004) 283: 49–57
DOI 10.1007/s00396-004-1088-1

ORIGINAL CONTRIBUTION

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Mechanistic studies on particle nucleation in the batch emulsion polymerisation of *n*-butyl acrylate containing multifunctional monomers

Received: 8 September 2003
Accepted: 20 January 2004

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Abstract This paper reports the mechanistic details concerning the synthesis of crosslinked poly(*n*-butyl acrylate) dispersions intended to be used as seeds in the preparation of core-shell emulsions. The influence of crosslinking comonomers and the amount and type of surfactants on the kinetics, particle nucleation, particle size and particle size distribution in the batch emulsion polymerisation of *n*-butyl acrylate (BA) is explored. In the case of EGDA (ethylene glycol diacrylate) crosslinker the particle number decreased with increasing crosslink density, whereas the opposite trend was observed in the case of *m*-diisopropenylbenzene (*m*-DIPB) in the presence and absence of the surfactant sodium dodecyl sulfate (SDS). The observed behaviour is mainly attributed to the variation in the aqueous phase kinetics caused by the water solubility of the comonomer, which influences the formation rate of precursor particles during the nucleation stage. Only for the less water soluble crosslinker, DIPB, could the increase of particle number be explained within the Smith–Ewart theory by assuming prolonged nucleation due to reduced swelling of growing particles with monomer as a result of the crosslinking reaction.

Keywords Particle nucleation · Emulsion copolymerisation · *n*-Butyl acrylate · Multifunctional monomers · Particle size distribution

Abbreviations *EGDA*: ethylene glycol diacrylate · *m-DIPB*: *meta*-diisopropenylbenzene · *SDS*: sodium dodecyl sulfate · *PBA*: poly(*n*-butyl acrylate) · *AFFF*: asymmetric field flow fractionation · *MALLS*: multiangle laser light scattering · *CMC*: critical micelle concentration

Introduction

Emulsion copolymerisation involving multifunctional monomers is an important process to produce crosslinked microgel particles useful in various applications like surface coatings, impact modification of brittle thermoplastics, adhesives and various medical applications [1, 2]. Crosslinked particles are also used in the preparation of structured core-shell emulsions with the objective of either controlling the morphology [3] or to modify the product properties [4, 5, 6]. Understanding of the particle formation process is crucial to control the final product properties and to avoid secondary particle formation when employed in the design of core-shell systems.

Nucleation leading to particle formation in emulsion polymerisation is a complex process, for which definitive predictions as to the dominant mechanism for a specific system are still awaited. It is now well accepted that the Smith–Ewart (SE) theory [7, 8] can successfully describe the styrene emulsion polymerisation, whereas for more water soluble monomers, such as vinyl acetate, the SE theory does not apply [7, 8]. The current paper is concerned with butyl acrylate, which is an industrially important monomer. Its aqueous solubility is slightly higher than that of styrene. Owing to the industrial importance of butyl acrylate, many studies have been reported in recent years on its emulsion polymerisation [9, 10, 11, 12, 13, 14]. These studies, however, mainly deal with the homopolymerisation of butyl acrylate. To our knowledge, only a limited number of studies have been reported on the emulsion copolymerisation of *n*-butyl acrylate with multifunctional monomers in the presence of surfactant [15, 16, 17], and none for the surfactant-free case. Such studies are important as it has been shown [18] that the addition of a comonomer which differs in water solubility from the monomer may lead to a mechanistic change in comparison to homopolymerisation.

The present paper addresses this issue and forms part of a project concerned with studying the structure–property relationship in film-forming composite dispersions. For this purpose seed emulsions with varying characteristics such as size and crosslinking were required. To meet this objective it was imperative to understand the particle nucleation of *n*-butyl acrylate (BA) in the presence of multifunctional comonomers such as ethylene glycol diacrylate (EGDA) and *meta*-diisopropenylbenzene (*m*-DIPB), which differ significantly in their water solubilities relative to BA, so as to prepare seed dispersions with varying particle size.

Experimental

Materials and methods

n-Butyl acrylate was obtained from Merck, Darmstadt, Germany. The crosslinking agents ethylene glycol diacrylate (EGDA) and meta-diisopropenylbenzene (*m*-DIPB) were obtained from Aldrich. The monomers and crosslinking agents were distilled under vacuum in a nitrogen atmosphere and then stored at −18°C until use.

Potassium peroxodisulfate ($K_2S_2O_8$) from Aldrich was used as obtained as an initiator. A 70% aqueous solution of the surfactant Triton X-305 (from Merck, Darmstadt, Germany) was employed. It contains an average number of about 30 ethylene oxide units as the hydrophilic part. Sodium dodecyl sulfate (SDS) supplied by SERVA Finebiochemika, Heidelberg, Germany was purified by recrystallisation from ethanol. Deionised water from a Millipore unit was used in all polymerisation experiments after filtration through an ultra filtration unit of 0.1-µm pore size.

Polymerisations were carried out in 250-mL round-bottomed flask fitted with a Teflon-glass stirrer, a gas bubbler and a reflux condenser. Care was taken to ensure that the stirrer was at a constant distance from the bottom of the flask, usually about 1 cm.

Preparation of latexes

The seed emulsions were prepared from butyl acrylate through a batch emulsion polymerisation process. All the polymerisations were run for 24 h at 78°C. At the end of the reaction emulsions were filtered through a 0.25-µm nylon filter to remove any coagulum. Samples were prepared with varying crosslink densities, crosslinking agents and also with surfactants. A typical recipe used for the synthesis is given in Table 1.

For the kinetic studies separate experiments were carried out. During polymerisation, 1–2 mL of the sample was withdrawn from the reaction flask by using a glass pipette, and the reaction was quenched by addition of a few mg of hydroquinone. The samples were analysed for particle size and solids content. The gel content of the various fractions was determined by extraction with tetrahydrofuran (THF).

Colloidal characterisation

Dynamic light scattering

The particle size of the dispersions was determined by dynamic light scattering. The measurements were performed with an ALV 5000 correlator from ALV, Langen, and a standard optical set up with an Nd–YAG solid-state ring laser unit (DPSS-50; COHERENT) emitting light at a wavelength of 532 nm. The results were analysed by using the cumulant method, yielding the hydrodynamic radius (R_H) [19]. The particle number of the colloids was then calculated by using the following expression [20, 21], assuming that the density of the polymer emulsion is 1 g mL^{-1}:

$$N\mathrm{p} = \frac{6 \times 10^{21}\mathrm{SOC}}{\pi D_\mathrm{p}^3 d}. \tag{1}$$

Here N_p is the particle number per cubic centimetre (cc), D_p is the average particle diameter in nm, SOC is the solid content in g mL^{-1} and d is the polymer density in g mL^{-1}.

In cases where a surfactant was used, the surfactant coverage on the particle surface was calculated from the particle size data by using the following relationship:

$$\chi = \frac{F\langle R\rangle \rho_\mathrm{p} a_\mathrm{m} N_\mathrm{A}}{3M,\mathrm{emul}}. \tag{2}$$

where χ is the percent surfactant coverage, F denotes the mass ratio of emulsifier to monomer, $< R >$ is the average particle radius, M_emul is the emulsifier molecular weight, ρ_p is the polymer density, a_m gives the area occupied by a surfactant molecule on the particle surface and N_A is Avogadro's constant.

Table 1 Typical recipe used for the preparation of poly(*n*-butyl acrylate) seed dispersions containing multifunctional monomers

Ingredients	Weight (g)
Deionised water	100
n-Butyl acrylate	10
Crosslinker (*m*-DIPB or EGDA)	0.063–0.6663 (variable)
Surfactant (SDS or Triton X-305)	Variable
Initiator ($K_2S_2O_8$)	0.090

Temperature 78°C, 300 rpm, 24 h

Asymmetric field flow fractionation

The particle size distribution of the dispersions was obtained with an asymmetric field flow fractionation unit (AFFF, CONSENXUS), coupled with a multiangle laser light scattering set-up (MALLS) [22]. In this method, separation is effected according to particle size by competing crossflow through a membrane and Brownian diffusion of the particles. Further experimental details are given elsewhere [23]. The data analysis and interpretation is achieved by using ASTRA Software (Version 4.70). In principle the radii distribution curves obtained from an FFF unit with MALLS give the fraction of the material with a particular radius. These distributions are of two kinds: cumulative and differential. The cumulative distribution is defined to be the weight fraction of sample having radii less than a specified radius (R).

From the data the radius, distribution graphs and polydispersity can be calculated. The cumulative distribution is given by

$$W(R) = \sum_{R'<R} C_{R'} \Big/ \sum_{\text{all } R'} C_{R'} \qquad (3)$$

where $C_{R'}$ is the mass concentration (derived from light scattering signal) for the slice having radii R'.

The polydispersity can be obtained from AFFF measurements as

$$\text{polydispersity} = \frac{R_{90} - R_{10}}{R_{50}}, \qquad (4)$$

where $R_{10,}$ R_{50} and R_{90} are the mass fractions at 10%, 50% and 90%, respectively.

Results and discussion

In the present work we have investigated the particle nucleation process in the emulsion polymerisation of *n*-butyl acrylate in the presence of two different multifunctional comonomers, namely ethylene glycol diacrylate and *m*-diisopropenylbenzene. To investigate the effect of crosslinker concentration on particle nucleation, dispersions were prepared at different crosslinker concentrations. To study the effect of surfactants, dispersions were also prepared by using the surfactants sodium dodecyl sulfate (SDS) and Triton X-305. The particle composition and other characteristics of the colloidal dispersions are given in Table 2. The following general features can be noticed: for particles for which EGDA was used as crosslinker, the average latex particle radius increases with increasing crosslinker concentration in the preparation of seed emulsions without surfactant from 111 nm at a crosslinker concentration of 0.5 mol% to 162 nm at 4.8 mol%. The same general trend was seen when SDS was employed as surfactant. However, the average particle size was significantly reduced and the increase was less pronounced with increasing crosslinker content (an increase of about 12% as compared to about 50% without surfactant).

In all the reactions without surfactant, some solid polymer swollen with the monomer was found enveloping the stirrer blade at the end of the reaction. The amount of this coagulum was found to increase with increasing crosslinker concentration, indicating a concomitant decrease of colloidal stability. The observed decrease in conversion (cf. Table 2) may, therefore, be attributed mainly to coagulum formation at later stages. For example, in the case of seed emulsion prepared with 4.8 mol% EGDA, the maximum conversion achieved was only 93%, whereas with 0.5 mol% crosslinker the conversion was 97% under surfactant-free conditions.

Table 2 Particle composition data for poly(*n*-butyl acrylate–comonomer) dispersions

Sample code	Surfactant used[a] ($\times 10^3$ mol dm^{-3})	Crosslinker[b] ($\times 10^3$ mol dm^{-3})	Conversion (%)	Hydrodynamic radius (R_H)[c] (nm)
Ce	–	–	97.5	141
Ce 1	–	E – 4.32	97	111
Ce 2	–	E – 5.56	94	123
Ce 3	–	E – 7.78	96	136
Ce 4	–	E – 19.2	78	154
Ce 5	–	E – 39.06	93	162
Ce 6	S –9.54	E – 4.04	98	32
Ce 7	S –9.64	E – 5.56	99	34.5
Ce 8	S –9.86	E – 7.82	97	35
Ce 9	S –9.54	E – 39.06	98	36
Ce 10	S –9.74	D – 3.91	99.5	31
Ce 11	S –9.74	D – 7.91	99	30
Ce 12	S –9.58	D – 20.41	99	29
Ce 13	S –9.47	D – 39.11	97	28
Ce 14	–	D – 4.03	99	122
Ce 15	–	D –8.14	99	115
Ce 16	–	D – 20.68	98	110
Ce 17	–	D –39.47	99	104
Ce 18	T –1.15	E – 8.09	99	154
Ce 19	T –7.17	E – 7.82	76	72
Ce 20	T –14.2	E – 8.40	98	44

[a] S = SDS; T = Triton X-305
[b] E = EGDA; D = *m*-DIPB
[c] From dynamic light scattering

Coagulum formation is also observed, but to a lesser extent, in the case where surfactant (SDS) was present above the critical micelle concentration.

Coagulation of precursor particles during particle growth is expected to increase the final particle size (the remaining monomer being shared between fewer particles). The reason for the origin of the observed increase in particle size with increasing crosslinker concentration becomes apparent when one looks at the particle number density (N_p), which was calculated by Eq. 1, and where the effect of decreasing conversion is corrected for by use of the solids content. The influence of EGDA crosslinker on the particle number density of the dispersions prepared without any surfactant and using SDS as surfactant is compared in Fig. 1.

In both cases a decrease of N_p with increasing crosslinker concentration is observed, the effect being again more pronounced in the surfactant-free dispersion (decrease by about 25% with SDS and by about 75% without). Disregarding quantitative differences, both types of dispersions show the same qualitative behaviour, which indicates that the major reason for the observed increase of particle size is a reduction of the particle number density. This implies that the crosslinker does not simply act as a comonomer, which would leave the particle number essentially constant, but seems to influence the particle nucleation mechanism itself.

The results observed with the other bifunctional monomer, *m*-diisopropenylbenzene (DIPB), suggest a different behaviour. All the experimental conditions were the same as those employed in the butyl acrylate–ethylene glycol diacrylate system. We observe features opposite to those in the case of the BA–EGDA system. The particle radii were found to slightly decrease with increasing crosslinker concentration. The effect was similar in the surfactant-free case (14%) and in the presence of SDS (10%), comparable in magnitude to the change of particle size in the BA–EGDA system with SDS. Coagulum formation was negligible and conversion was generally higher than in the BA–EGDA system (cf. Table 2), amounting to 99% in most cases with no significant difference between surfactant-free and SDS-containing dispersions. Obviously, here the surfactant leads only to an overall reduction of particle size and does not seem to affect the particle nucleation mechanism. This is also seen in Fig. 2, where the variation of the particle number with the concentration of the bifunctional monomer DIPB in the initial monomer feed is shown.

Opposite to the BA–EGDA system, one observes an increase of particle number density on increasing the crosslinker concentration. Besides a difference in absolute particle numbers the same trend is seen for surfactant-free and SDS-containing dispersions.

Thus, it is obvious to assume that the observed decrease of conversion is mainly due to coagulum formation. To distinguish if the coagulum formation is inherent in the nucleation process itself, as observed by Hansen and coworkers [24, 25], or due to mechanical instability during the later stages of the reaction (due to shearing), a kinetic study of the polymerisation was performed for selected systems, ce, ce3 and ce15 (cf. Table 2). The results are plotted in Fig. 3. It can be seen that in the case of the BA–EGDA system, the particle number showed a decrease from the initially higher value when plotted as a function of time. These changes occur mainly during or just after the nucleation period. The same behaviour is observed for *n*-butyl acrylate

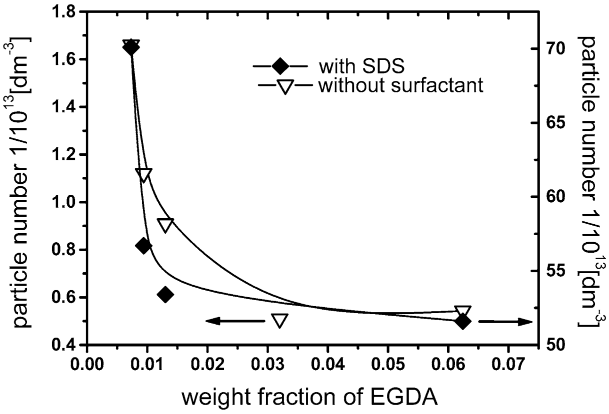

Fig. 1 Variation of particle number (per dm^3) with ethylene glycol diacrylate (EGDA) crosslinker concentration in the batch emulsion polymerisation of *n*-butyl acrylate at 78°C with 3.33×10^{-3} mol dm^{-3} potassium persulfate (∇ surfactant-free, and ◆ in the presence of 9.7×10^{-3} mol dm^{-3} SDS). The *lines* are guides to the eye, and the *arrows* indicate the appropriate scale

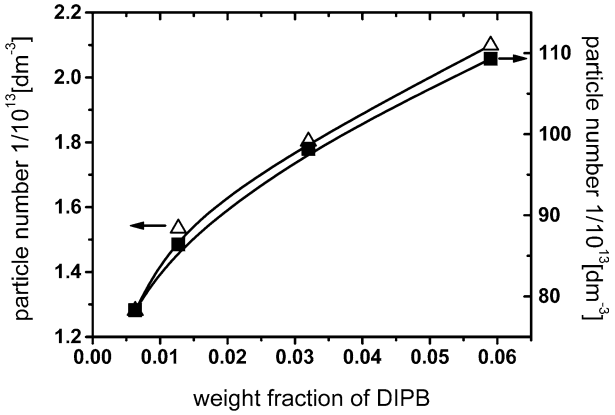

Fig. 2 Variation of particle number (per dm^3) with *m*-diisopropenylbenzene (DIPB) crosslinker concentration in the batch emulsion polymerisation of *n*-butyl acrylate at 78°C with 3.33×10^{-3} mol dm^{-3} potassium persulfate (Δ surfactant-free, and ■ in the presence of 9.74×10^{-3} mol dm^{-3} SDS). The *lines* are guides to the eye, and the *arrows* indicate the appropriate scale

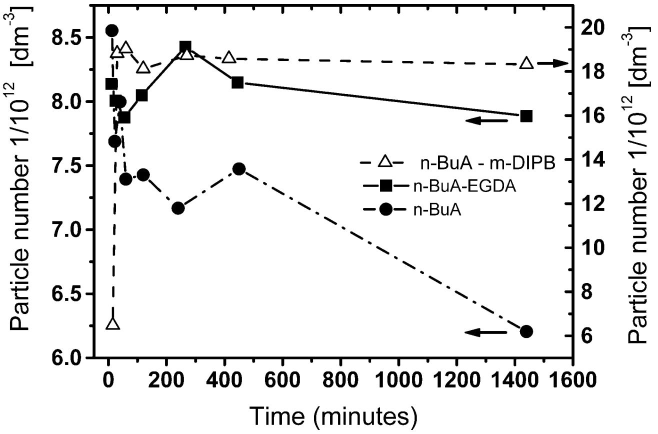

Fig. 3 Kinetic curves showing the particle nucleation in the surfactant-free batch emulsion polymerisation of *n*-BuA (●), *n*-BuA–EGDA (■) and *n*-BuA–*m*-DIPB (Δ) systems at 78°C with 3.33×10^{-3} mol dm^{-3} persulfate initiator. The *lines* are guides to the eye, and the *arrows* indicate the appropriate scale

without any crosslinker. In the case of the BA–DIPB system, the particle number increases during the nucleation stage and remains nearly constant during the full conversion. In all systems, some coagulation owing to instability is observed towards the later stages of the reaction, the effect being negligible in case of the BA–DIPB system.

The gel content of the samples, which were collected at different time intervals and determined by extraction with THF, provides additional information as to how the crosslinker influences the nucleation mechanism. In the case of the BA–EGDA system the gel fraction at 10 min after the start of the reaction was 74%, which increased to 85% and 93% at 55 min and at the end of the reaction, respectively. In the case of the DIPB system the increase in the gel fraction was slower. The value was 29% after 30 min, 73% after 120 min and 76% at 415 min. These results show that a crosslinked structure is formed much faster in the case of the BA–EGDA system relative to the BA–DIPB system.

The influence of the crosslinkers, as shown in Figs. 1 and 2, is at first sight surprising. In particular, the observation of a similar trend in the variation of particle number with and without surfactant is not easily understood, as the mechanistic processes are generally believed to be quite different in the two types of emulsion polymerisation [26, 27]. Nevertheless, these findings can be rationalized within the currently accepted mechanistic models of emulsion polymerisation: the Smith–Ewart theory [7, 27] for the case with surfactant above CMC, and homogeneous coagulative nucleation theory [27, 28] for surfactant-free emulsion polymerisation. We address three features in which the crosslinker molecules differ from the monomer—the higher reactivity of the crosslinker molecules, the different water solubilities and their ability for network formation. A few studies on the effect of crosslinker on particle nucleation above CMC have been reported [15, 16, 17]. In contrast, to the best of our knowledge, comparable studies are missing for surfactant-free emulsion polymerisation. Therefore, we will start our discussion with the experiments above CMC.

Effect of crosslinker in the presence of SDS above CMC

In the presence of surfactant above its CMC the emulsion polymerisation is generally believed to proceed according to a micellar mechanism, which is described in the well-known Smith–Ewart theory [7]. The theory predicts a power law dependence of particle number density (N_p) on initiator concentration [I] and the surfactant concentration [S] [27]:

$$N_p = k\left(k_d[\mathrm{I}]/\mu\right)^{2/5}\left(a_s[\mathrm{S}]\right)^{3/5}, \qquad (5)$$

where k is a numerical constant of order of 1, k_d is the initiator decomposition rate and a_s is the adsorption area per surfactant molecule on the surface of polymer particles. The volumetric growth rate per particle μ in interval I is, in turn, linearly dependent on the propagation constant of the polymer (k_p) and the monomer concentration in the particles (C_p) (i.e. $\mu \propto k_p C_p$) [27]. The applicability of the Smith–Ewart (SE) theory to the emulsion homopolymerisation of butyl acrylate was studied by Sajjadi and Brooks [8]. They found that for this sparingly water soluble monomer (water solubility only 50% higher than styrene) the particle formation kinetics obey the SE theory above and slightly below CMC. However, these authors discussed the possibility that homogeneous nucleation may play a role as well, as they did not observe a change of slope of the N_p versus [S] curve at the CMC. Further studies by Capek and Potisk [16] showed that initiation in the aqueous phase is also accepted for sparingly water soluble monomers like BA; the number-average degree of polymerisation of BA oligomers necessary for separation from the aqueous phase was about 13.

The results observed for the BA–DIPB system are in fact similar to earlier studies [15, 16, 17] for different systems. Similar to our work, an increase of the particle number density on increasing the crosslinker content in the monomer mixture was observed. In all cases this effect was attributed to a reduction of the monomer concentration in the growing particles due to a decrease of the swelling ability on increasing the internal crosslink density which results in a reduced volume growth rate (μ) and a concomitant increase of the particle number density, as can been seen from Eq. 5. Additionally it has been shown theoretically [29] that in emulsion polymerisations with multifunctional monomers the crosslinking density of the produced polymers is high from the very beginning of the reaction, so that the absorption of monomer in the polymer particles could be limited even in the particle nucleation stage (interval I).

In the case of the BA–EGDA system a decrease of N_p can occur (according to Eq. 5) if the volumetric growth rate is high. This could happen if an increase of the propagation constant (k_p) occurs, which then overcompensates for the effect of the decreased monomer concentration in the particles (C_p). From emulsion copolymerisation studies (e.g. see ref. [18]) it is known that the average propagation constant in the particle increases when a monomer is copolymerised with a comonomer which has a higher k_p and vice versa. It is reasonable to assume that the presence of the second vinyl group of the crosslinker increases k_p (if defined per monomer) by a factor of about two relative to the related monomer [30]. But since this increase is common to all crosslinkers, this alone cannot explain the observed difference between EGDA and the other multifunctional monomers. One would have to assume that the propagation constant of EGDA is much higher than that of BA, whereas this is not the case for the other multifunctional monomer like *m*-DIPB. In fact such a difference in reactivity between the crosslinkers has been reported [31, 32]. The decrease of N_p with increase of crosslinker amount observed with EGDA is not a fortuitous result, as similar observations have been made earlier with another monomer, *t*-butyl acrylate, again using EGDA and DIPB as comonomers [33].

Another simple explanation emerges if one compares the water solubilities of the monomers BA (6.4×10^{-3} mol L^{-1} [27]; 1.1×10^{-2} mol L^{-1} [16]) with those of the crosslinkers DIPB (4×10^{-5} mol L^{-1} [16]) and EGDA [$\approx5\times10^{-2}$ mol L^{-1}; estimated on the basis of a comparison between divinylbenzene (DVB) (5×10^{-4} mol L^{-1} [16]) and DIPB, as the actual value was not known]. This indicates that in the BA–DIPB system, the crosslinker was significantly less water soluble than the monomer. A similar effect was reported in the emulsion copolymerisation of BA with DVB and acrylonitrile (AN) [16]. There, it was concluded that application of the DVB monomer favours nucleation in micelles (assuming that homogeneous nucleation is predominant in pure BA), whereas copolymerisation of the hydrophilic AN favours homogeneous nucleation. Thus, it seems reasonable to assume that in our study of the BA system, where the surfactant concentration chosen was just slightly above CMC, micellar and homogenous nucleation might be balanced such that the copolymerisation of a more water soluble comonomer like EGDA tips the balance over in favour of homogeneous nucleation, and the high radical concentration (probably rich in crosslinker molecules) in the aqueous phase favours coagulation, whereas the less water soluble crosslinker *m*-DIPB favour micellar nucleation.

Effect of crosslinker in surfactant-free systems

The particle formation in surfactant-free systems is generally explained by the model of homogeneous coagulative nucleation [27]. According to this theory the rate of particle formation [$\mathrm{d}(N_p/N_A)/\mathrm{d}t$ in molar units] is given by the total precursor particle formation rate [27]:

$$\frac{\mathrm{d}\left(N_p/N_A\right)}{\mathrm{d}t} = k_{p,aq}C_w[j_{crit}]. \qquad (6)$$

Here $k_{p,aq}$ denotes the propagation constant in the aqueous phase, C_w the concentration of the monomer in the water phase and $[j_{crit}]$ the concentration of oligomers of size j_{crit} (i.e. of degree of polymerisation sufficient for formation of precursor particles). The last of these depends on the value of j_{crit} and in a complicated manner on aqueous phase processes like entry, radical desorption and termination. One can expect that—all other conditions being constant—the steady-state concentration $[j_{crit}]$ of chains with critical degree of polymerisation will be smaller, the higher the value of j_{crit}. This line of argumentation has been used by Guo et al. [17] in the—to the best of our knowledge—only study of nucleation in emulsion copolymerisation with multifunctional monomers (MMA/EGDMA) significantly below CMC to explain the observed increase of N_p with increasing crosslinker content in the monomer feed. The existence of EGDMA in the water phase leads to oligomeric chains that are more hydrophobic, thus reducing the critical chain length for precipitation. Accordingly, one would expect an increase of N_p when BA is copolymerised with the less water soluble crosslinker DIPB and a decrease if the more water soluble crosslinker EGDA is used, as was indeed observed in our experiments (cf. Figs. 1 and 2).

Further, the role of aqueous phase kinetics affecting particle nucleation was highlighted in another study by Schoonbrood et al. [18]. They showed that a weight fraction of styrene (ST) in the aqueous phase as low as 0.036 decreases the average $k_{p,aq}$ in methyl acrylate(MA)/ST emulsion copolymerisation to 740 L mol^{-1} s^{-1} as compared to the value of 10,700 L mol^{-1} s^{-1} for pure MA. In general, one can expect that more water soluble monomers have higher propagation constants than less water soluble monomers. Thus, the actual behaviour of N_p (according to Eq. 6) is determined by the competing effects of an increase of $[j_{crit}]$ and a decrease of C_w and $k_{p,aq}$ (and vice versa) due to copolymerisation of a less (more) water soluble crosslinker. In our case the observation that addition of the less water soluble DIPB increases

N_p, whereas the more water soluble EGDA leads to a decrease, seems to imply that the effect on j_{crit} (i.e the decrease or increase of the critical degree of polymerisation) is the dominating one.

One could also imagine, as the reason for enhanced coagulation, that the crosslinking reaction reduces the mobility of the polymer chains within the particles such that the reduced number of initiator-derived sulfate groups can migrate to the particle surface. As a consequence, the surface charge density is reduced as compared to the uncrosslinked case leading to an enhancement of precursor coagulation and, hence, to a reduction of the particle number with increasing crosslinker concentration. That coagulation indeed takes place during the particle formation stage in the case of the BA–EGDA system is clear from Fig. 3. In contrast, such an effect could not be detected in the BA–DIPB system: the absence of such an effect in this system was inferred from the observation [31, 32] that the reaction of the second double bond is significantly delayed in the case of DIPB as compared to other multifunctional monomers. This is also supported by our observation that the gel content increases much slower in the BA–DIPB system when compared to BA–EGDA system.

Effect of added surfactant

Comparing the effect of surfactant on particle nucleation, one sees that the particle number is lowest (large particle size) for surfactant-free and non-ionic-surfactant-based seed emulsions as compared to the system containing anionic surfactant (cf. Table 2).

The anionic surfactant SDS was used at a concentration slightly above the CMC (2.6 g L^{-1}), as the particle number produced will be maximum at the concentrations around the critical micelle concentration (CMC) [26]. The effect of the non-ionic surfactant on the particle number was less dominant when used at its CMC of 0.12 g L^{-1} (ce18; Table 2). In other words, in the case of the non-ionic surfactant no appreciable increase in the particle number (or decrease of particle size) was noticed in comparison to the anionic surfactant. To see the effect of Triton X-305 in reducing the particle size, emulsions were prepared at different concentrations of surfactant. With increasing concentration of Triton X-305 the particle number increases, as can be deduced from the observed decrease in the particle size (cf. Table 2), and the effect is shown graphically in Fig. 4.

To study the surfactant influence on polydispersity, the particle size distribution of the dispersions was determined by AFFF–MALLS. The effect of the surfactant type is shown in Fig. 5. The surfactant-free system is found to be monodisperse, as reported earlier by other investigators [27] who attributed this mainly to the high temperatures used in the polymerisation. The polydispersity was calculated from the distribution curves by using Eq. 4. In the case of surfactant-free systems the polydispersity is nearly 1%. When an anionic surfactant was used the polydispersity goes up to 17.89%, and with the non-ionic surfactant the value is 7.6%.

The effect of increasing concentrations of Triton X-305 on the observed particle size distribution is shown in Fig. 6. The polydispersity increases from 7.6% to 27% when the concentration is increased from 0.8 mM to 4.994 mM and then to 29% at 9.97 mM. The increase in distribution is less marked at higher concentration of Triton X-305. This may be a consequence of coagulum formation leading to additional polydispersity, as indi-

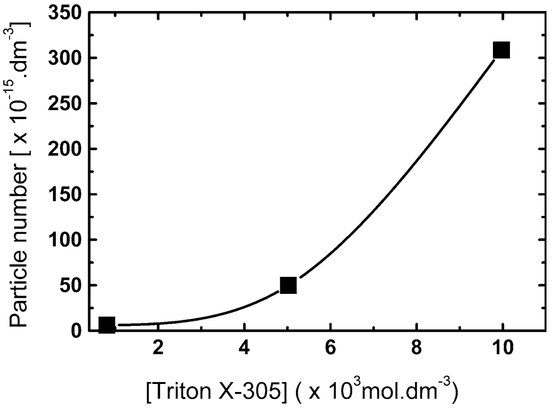

Fig. 4 Final particle number for batch emulsion polymerisation of *n*-butyl acrylate as a function of Triton X-305 concentration. Temperature 78°C, EGDA crosslinker = 8×10^{-3} mol dm^{-3} and [I] = 3.33×10^{-3} mol dm^{-3} persulfate initiator. The *line* is a guide to the eye

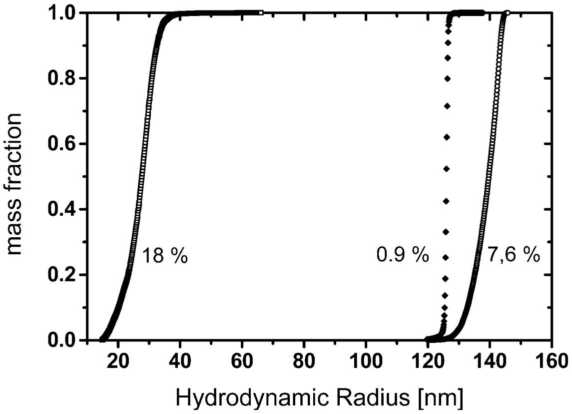

Fig. 5 Variation of particle size distribution in the seed emulsions prepared with SDS (ce8), without surfactant (ce) and with Triton X-305 (ce18) surfactant (from *left* to *right*) from *n*-butyl acrylate at 78°C with 3.33×10^{-3} mol dm^{-3} potassium persulfate. The *numbers* next to the *curves* give the polydispersity in percent as calculated via Eq. 4

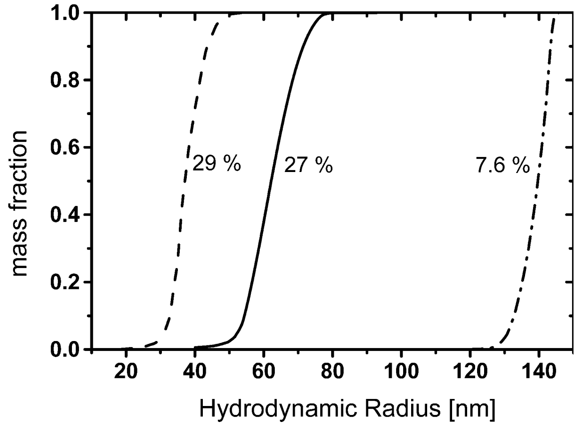

Fig. 6 Effect of varying Triton X-305 surfactant concentration on the particle size distribution of the seed emulsion prepared from *n*-butyl acrylate at 78°C with 3.33×10^{-3} mol dm^{-3} potassium persulfate and 8×10^{-3} mol dm^{-3} ethylene glycol diacrylate cross-linker. Surfactant concentrations (from *left* to *right*): 9.99 mM (ce20), 4.999 mM (ce19), 0.806 mM (ce18). The *numbers* next to the *curves* give the polydispersity in percent as calculated via Eq. 4

cated by the decrease in conversion at 4.99 mM Triton X-305 (cf. Table 2). This effect is typical of the longer chain length surfactants when the concentration of the surfactant exceeds the critical coagulation concentration [34]. At higher concentrations restabilisation occurs.

A similar overall increase of polydispersity with a bimodal particle size distribution was found in the homopolymerisation of *n*-butyl acrylate by Özdeger et al. [35] when increasing the Triton X-405 concentration. To further elucidate the influence of surfactants on the particle size distribution the surfactant coverage was calculated from the particle size and reported values of the area per surfactant molecule [36, 37] using Eq. 2. The values calculated along with the polydispersity are shown in Table 3. For both anionic and non-ionic surfactants the coverage is below 100% at their respective CMCs. The significant increase in polydispersity on increasing the Triton X-305 concentration coincides with surfactant coverage above 100%. In this case free surfactant may be present and lead to a prolonged nucleation stage or even to secondary nucleation, as indicated by bimodal distributions in earlier studies [35].

Conclusions

The addition of a crosslinking comonomer strongly influences the particle number density (N_p), and hence the particle radii, in the emulsion copolymerisation of butyl acrylate (BA). This led to a decrease of N_p in the case of the multifunctional comonomer ethylene glycol diacrylate (EGDA), and an increase of N_p if 1,3-diisopropenylbenzene (DIPB) was employed. The same trends are observed irrespective of whether the polymerisation is carried out in the absence of the surfactant SDS or at SDS concentrations slightly above CMC; however, these trends are less pronounced in the presence of SDS.

Table 3 Calculation of the surfactant coverage for the various emulsions along with the calculated polydispersity values

Sample code	Surfactant used	Surface coverage[a] (%)	Polydispersity[b] (%)
Ce2	–	–	0.87
Ce9	SDS	40	17.89
Ce18	TritonX-305	38	7.6
Ce19	Triton X-305	110	27
Ce20	Triton X-305	134	29

[a] Value calculated using Eq. 2
[b] Value calculated using Eq. 4 from FFF experimental data

In the case of the less water soluble crosslinker DIPB with SDS surfactant, the observed increase of the particle number could be explained on the basis of Smith–Ewart case II kinetics, as a consequence of a decrease of the particle growth rate. This decrease is caused by a reduced monomer swelling ratio and a concomitant prolongation of the nucleation due to the crosslinking reaction, as discussed in the literature for other monomer–crosslinker systems [15]. In contrast, addition of the more water soluble crosslinker EGDA most likely changes the nucleation process from the micellar to the homogeneous coagulative mechanism. Here, the observed decrease of N_p can be attributed to an increase of j_{crit}, the minimal degree of polymerisation necessary to form a precursor particle.

In an analogous manner the increase of particle number due to addition of DIPB in the absence of surfactant can be interpreted as a consequence of a decrease in j_{crit} owing to the copolymerisation of BA with a less water soluble comonomer. In the absence of surfactant the coagulation tendency may be reinforced by the presence of EGDA, as the crosslinking reaction tends to keep the initiator-derived charges from migrating to the particle surfaces, thus additionally destabilizing the precursor particles, as can be deduced from the time evolution of N_p. This effect seems to be missing in the case of DIPB, which is consistent with the fact that the crosslinking reaction proceeds much slower than in the case of EGDA.

The main effect of the surfactant is to counteract the coagulation of precursor particles by stabilizing smaller and, hence more numerous, nuclei as compared to the surfactant-free case.

Acknowledgments The financial support from DAAD (Deutscher Akademischer Austausch Dienst to K.I. Suresh in the form of a Sandwich model fellowship under CSIR-DAAD Exchange program is gratefully acknowledged. Thanks are due to Dr Andrei Veniaminov for careful reading and suggestions for the manuscript.

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