Macromol. Symp. ***150,*** *1–12 (2000)*

Nucleation in Heterophase Polymerizations

Klaus Tauer *, Carsten Schellenberg, Arvid Zimmermann

Max Planck Institute of Colloids and Interfaces

Am Mühlenberg, D 14476 Golm, Germany

SUMMARY: It is desirable to assess whether the final particle number in heterogeneous polymerizations is predetermined by the number of monomer droplets. If this is really the case nucleation occurs very smoothly via a polymer in monomer solution where the kinetically important step is the initiation reaction inside the droplets. However in the case of emulsion and dispersion polymerizations the nucleation step is a sharp phase transition when the free polymer phase is formed in the continuous phase. This process can be described generally with the classical nucleation theory although it is today not yet possible to give quantitative explanations for some new experimental results. These new experimental results prove the strong influence the kind of the reactor material as well as the stirrer speed has on particle nucleation and final latex properties.

Introduction

The technical term “Heterogeneous Polymerization” indicates not a single polymerization technique but is much more a generic term for a variety of heterophase polymerization techniques; for instance suspension, microsuspension, dispersions, miniemulsion, emulsion, and microemulsion polymerization. So the question arises whether or not there is something general about particle nucleation? The common feature is the formation of a new phase, the polymeric phase. This is true independent of whether or not the final polymer particles are preformed as monomer droplets. In suspension, microsuspension, miniemulsion, and microemulsion polymerization it is assumed that the reaction proceeds almost exclusively inside preformed monomer droplets. In such a situation the formation of a polymer phase takes place very smoothly as first a polymer in monomer solution is formed and only at higher conversions are solid polymer particles generated. In suspension and microsuspension polymerizations one can correlate the point of particle identity (where

© WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2000 CCC 1022-1360/00/$ 17.50+.50/0

breakage and formation of droplets due to shear forces stops) with particle formation. In the case of *ab initio* emulsion and dispersion polymerizations particle formation occurs at the very beginning of the reaction as a sharp transition which is independent of the presence or absence of monomer droplets. Table 1 classifies heterophase polymerizations with respect to the kind of formation of the polymer phase.

Table 1. Discrimination of nucleation phenomena in heterophase polymerizations

Polymerization technique	*Monomer*	*Nucleation phenomenon*
Ab initio emulsion or dispersion	Feed or droplets [a)]	Phase formation at the very beginning of the polymerization
Suspension and microsuspension	Stable monomer droplets under the influence of shear forces	Point of particle identity and polymer solubility in the monomer determines phase formation [c)]
Microemulsion and miniemulsion	Stable droplets also in the absence of shear forces [b)]	Polymer solubility in the monomer determines phase formation [c)]
Seed techniques	Feed or droplets	Suppress phase formation

a) Note that the presence of a free monomer phase in the reactor is not necessary
b) Microemulsions are thermodynamically stable; miniemulsions are kinetically stable
c) It is assumed that reactions in the continuous phase are suppressed

With respect to nucleation, *ab initio* emulsion and dispersion polymerizations are the most exciting cases as the formation of the polymer particles starts from a homogeneous continuous phase. The aim of the paper is to report new experimental results with respect to the influence of the reactor material and the stirrer speed, respectively, on nucleation in *ab initio* emulsion polymerizations.

Results

To investigate nucleation in ab initio emulsion and dispersion polymerization is not only exciting but also challenging as it looks like these techniques conceal the secret of nucleation. Particle formation occurs not only at very low conversions but also very quickly. For example, during a surfactant-free emulsion polymerization of styrene the first particles have been detected at a solid content of about $2{,}1 \cdot 10^{-5}$ g per cm^3 water. After a pre-nucleation period of almost 430 s about $2 \cdot 10^{13}$ particles per cm^3 of water have been formed within less than 1 second [1, 2]. This corresponds to a nucleation rate of at least $3 \cdot 10^{-8}$ mol dm^{-3} s^{-1}. However, a direct experimental observation of the nucleation step is still an unsolved problem. This requires a fast method with a resolution in the range of milliseconds. Consequently, all nucleation models for emulsion polymerizations are based on experimental data obtained more or less far away from the nucleation point. Nevertheless, it was possible to verify experimentally essential predictions of the classical nucleation theory (CNT) like: a rapid increase in the particle number at the moment of nucleation, a poor reproducibility, surfactants and micelles play no direct role, but if surfactants are present nucleation takes place earlier [1]. Note, that the nucleation rate estimated above is almost three orders of magnitude greater than the rate predicted by a homogeneous nucleation theory of emulsion polymerization [3]. Furthermore, CNT predicts an influence of all kinds of interfaces present in the reaction system as heterogeneous nucleation occurs at lower activation energies than homogeneous nucleation [4]. In order to investigate the influence of interfaces aqueous phase polymerizations of methyl methacrylate (MMA) and styrene have been carried out in identical test tubes made of different materials (Duran® glass, stainless steel (st. steel), and Teflon®) [5]. The monomer concentration was chosen so low that no free monomer phase was formed. At the end of the reaction dynamic light scattering was used to check whether or not particles have been formed. Before starting these experiments all test tubes were treated with a potassium peroxodisulfate solution (2 g dm^{-3}) at 80 °C for 6 hours in order to clean the surfaces. Each polymerization recipe was repeated at least 10 times to get trustworthy results. Aqueous phase polymerizations have been attracting researchers continuously for more than 50 years in order to investigated the mechanism of emulsion polymerization [6-11]. However, to the best of the authors knowledge, this is the first report on systematic studies about the influence of chemically different interfaces (reactor materials) on aqueous phase polymerizations.

MMA polymerizations

The water solubility of MMA is so high [12] that polymerizations of aqueous solutions lead to polymer dispersions without any problems [10]. The results depicted in Figures 1 and 2 show that the reactor material has a pronounced influence on both the average particle size and the molecular weight (weight average M_W). In the case of the anionic initiator – emulsifier – system (IES) the observed dependencies show the expected behavior independent of the reactor material as D_V and M_W decrease with increasing SDS and KPS concentration respectively. Moreover, the products formed in the Teflon test tubes have the lowest D_V and M_W values whereas the glass reactor products possess larger particle sizes and higher molecular weights.

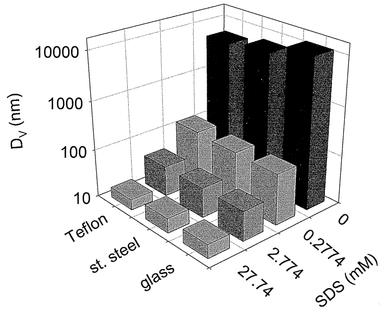

Fig. 1a Changes in D_V with the SDS concentration and reactor material (75 mM MMA, 3.7 mM KPS)

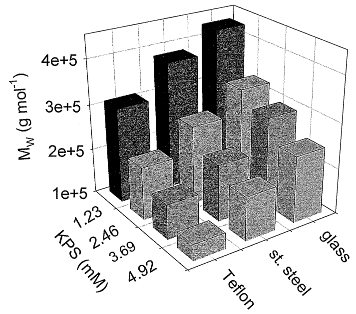

Fig. 1b Changes in M_W with KPS concentration and reactor material (75 mM MMA, surfactant-free)

If a cationic IES is used the situation is quite similar with respect to D_V. In contrast, M_W shows a slightly different pattern in dependence on the CTAB concentration and the reactor material (cf. Fig. 2b). But also in this case the material polymerized surfactant-free in the glass reactor has the highest molecular weight. A comparison between Figures 2a and 2b shows that with decreasing particle size the molecular weight also decreases.

Surfactant-free polymerization of aqueous MMA solutions is very sensitive to the KPS concentration and the reactor material (cf. Fig. 3). The DLS data show a very strong dependence on the KPS concentration. The largest D_V values were measured again in glass reactors at the highest KPS concentration of 4.92 mM. At this concentration the D_V value of the product from the Teflon test tube is 5520 nm ± 1600 nm and that of the glass reactor product is 12000 nm ± 2400 nm. These values indicate that the latexes are unstable. It is interestingly to note that a repeat of the glass reactor runs resulted in a D_V value of 12300 nm ± 3000 nm which is a remarkable reproducibility for flocculation. Indeed, cautious TEM investigations reveal firstly, that these latexes are flocculated and secondly, that in both cases the size of an individual particle is between 100 nm and 400 nm. At the lowest KPS concentration of 1.23 mM TEM pictures show individual particles with an average size that corresponds almost to the DLS results.

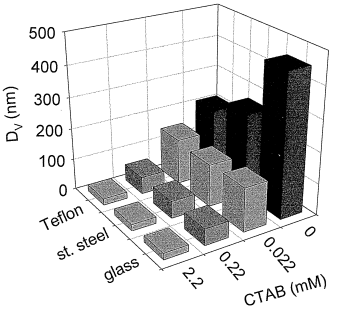

Fig. 2a Changes in D_V with reactor material and CTAB concentration; (75 mM MMA, 3.7 mM V50)

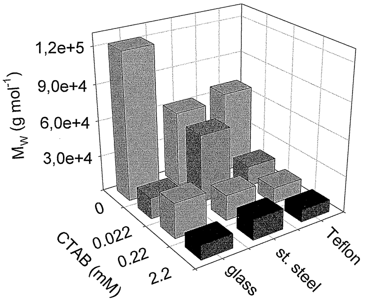

Fig. 2b Changes in M_W with reactor material and CTAB concentration; (75 mM MMA, 3.7 mM V50)

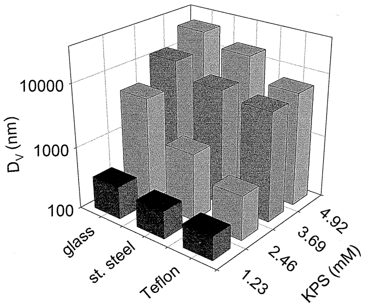

Fig.3 Change of D_V in dependence on reactor material and KPS concentration (75 mM MMA, surfactant-free)

This is real proof for the influence of the reactor material on the average particle size. The D_V values in the glass, stainless steel, and Teflon test tubes are 335 nm ± 23.5 nm, 278 nm ± 9 nm, and 241 nm ± 9 nm, respectively. Another interesting result is the strong influence of the reactor material on the flocculation of the latex particles at higher KPS concentrations. Alas, a satisfying explanation for this is today not possible.

Table 2. C^0_{app}-values (M) in dependence on IES and reactor material

Material	SDS-KPS	CTAB-V50
Glass	$1\ 10^{-9}$	$1.3\ 10^{-6}$
Stainless steel	$6\ 10^{-9}$	$4.5\ 10^{-6}$
Teflon	$5.7\ 10^{-8}$	$9.1\ 10^{-6}$

The influence of the reactor material can be quantified with the particle sizes from the surfactant-free runs and the corresponding experimentally determined log-log relationship between average particle size and surfactant concentration obtained, then an apparent zero-surfactant concentration (C^0_{app}) is calculated. C^0_{app} measures to what extent a particular reactor material influences the average particle size. The C^0_{app}-values summarized in Table 2 show that Teflon and a cationic IES support formation and stabilization of particles much more than an anionic IES and other materials, respectively. The large difference between anionic and cationic IES at zero or low surfactant concentration is due to the fact that surfaces in contact with water are generally negatively charged and hence interactions with cationic species are much stronger.

Styrene Polymerizations

In contrast to MMA the water solubility of styrene is much lower [13)] and hence, aqueous phase polymerizations of styrene must not inevitably lead to the formation of a polymer dispersion. Consequently, it is interesting to observe under which conditions nucleation occurs (cf. Table 3).

Table 3. Surfactant-free aqueous styrene polymerizations: D_V – values (nm) of final latexes versus kind of initiator and reactor material; initiator concentration 3.7 mM

Material / Styrene (mM)	PEGA200	KPS	V50
Glass / 0.6	941 ± 209	59.5 ± 15	0
Glass / 1.2	125 ± 24	94.3 ± 4.5	4070 ± 3100
Stainless steel / 0.6	565 ± 215	63.5 ± 15	0
Stainless steel / 1.2	538 ± 220	96.6 ± 5.3	0
Teflon / 0.6	0	0	0
Teflon / 1.2	763 ± 133	0	0

Again, the data in Table 3 reveal that polymerizations in Teflon tubes represent a special case as nucleation is hardly realizable under the particular experimental conditions [14)]. Also in the case of the cationic V50, particles have been detected only at the highest monomer concentration in glass tubes. These results prove the influence of the chemical nature of the oligomer end groups and again, of the reactor material on nucleation.

Another interesting fact is worthy of mention as compared with MMA. The aqueous styrene polymerization leads still at a monomer to KPS molar ratio of 0.16 to a latex whereas, in the case of aqueous MMA polymerizations already at a monomer to KPS molar ratio of 1.1 no particles have been detected. The reason for this difference is the different hydrophilicity of both oligomers which leads, the same end groups provided, to a different solubility and hence to a different critical nucleation concentration (CNC) of the oligomers.

KPS acts not only as initiator but also as electrolyte and CNT predicts that nucleation in aqueous polymerizations depends on both the chain length of the oligomers 1) and the electrolyte concentration 4). Consequently, whether or not nucleation occurs should also depend on the KPS concentration. Surfactant-free aqueous styrene (0.6 mM) polymerizations lead at a KPS concentration of 3.7 mM in glass and stainless steel reactors to particles with D_V – values of 59.5 nm ± 14.7 nm and 63.5 nm ± 15.3 nm, respectively. In contrast no particles have been detected in Teflon tubes at all concentrations and at KPS concentrations of 1.23 mM and 0.123 mM in all kinds of test tubes.

Another important question is concerning the role of surfactants in the nucleation process. If a constant styrene feed is ensured during the polymerization surfactants promote an earlier nucleation 1). However during the test tube experiments the styrene concentration is limited and so low that the CNC may not be reached (cf. Table 3). In no cases were particles observed at a styrene concentration of 0.6 mM in the presence of surfactants. The results for a styrene concentration of 1.2 mM in the presence of SDS and an initiator concentration of 3.7 mM are summarized in Table 4. A really strange pattern is observed besides the influence of the material, both types of initiators show an opposite behavior in dependence on the SDS concentration which obviously indicates special interactions between anionic (KPS) and nonionic (PEGA200) oligomers with SDS. At lower SDS concentrations the electrolyte character of KPS dominates the behavior.

The influence of surfactants on nucleation is not unambiguous as interactions with oligomers, initiators, and reactor materials have to be taken into consideration. Another action of the surfactants during the nucleation period is that their presence in the aqueous phase leads to an increase in the solubility of other organic products in water 15). This suggests that in some cases, in the presence of surfactants, no particles have been detected whereas

Table 4. D_V – values (nm) for aqueous styrene polymerizations in the presence of SDS

Reactor / Initiator	0.277 mM SDS	2.77 mM SDS	27.7 mM SDS
Glass / KPS	70.8 ± 10	28.5 ± 4.1	0
Glass / PEGA200	24.2 ± 3.2	43.8 ± 8.7	48.1 ± 8.8
St. steel / KPS	83.2± 3.7	43.7 ± 6.6	0
St. steel / PEGA200	26.1 ± 3.5	40.9 ± 3.7	55.9 ± 14.6
Teflon / KPS	67.7 ± 16.5	46.3 ± 7.2	307.4 ± 14.4
Teflon / PEGA200	0	0	61.3 ± 14.1

in the corresponding surfactant-free polymerizations nucleation has occurred. Consequently, surfactants cause an increase in the CNC and hence, under certain conditions (monomer starvation), their presence can even prevent nucleation.

In conclusion to this section, the reactor material can in different ways influence the aqueous polymerizations of styrene and MMA. One possibility is that surface impurities act as inhibitors during the polymerization. In that case one might also expect an influence on the final particle concentration as it was found for styrene emulsion polymerization in the presence of 9-vinyl anthracene as inhibitor 16). Another way how an interface can act during nucleation is that it can directly influence the nucleation step by changing the free activation energy of nucleation 4). The greater part of the results presented so far proves at least qualitatively the CNT although quantitative predictions are still not possible. It is worthy of mention that also other theoretical approaches can be used to explain at least parts of these results 1, 16). One reason for this situation is the complexity of the heterogeneous polymerization system about which all of the parameters that influence the final particle concentration are not known.

Influence of the stirrer speed

One among these influences is the stirrer speed (R_{pm}). Figures 4 and 5 show that R_{pm} has a distinct influence on the rate of polymerization (measured as heat flow, HF) as well as on the particle size and the number average molecular weight (M_N) 17). The increase in all three quantities with increasing R_{pm} is very pronounced. This is surprising as it is generally assumed that the stirrer speed is only of minor influence and modern textbooks even completely ignore this topic. However a few results are published indicating an influence if the inert gas for purging contains traces of oxygen as well as if a chain transfer agent has to diffuse out of the monomer droplets into the particles 18), if the monomer diffusion to the reaction loci is influenced [19)], or if the emulsifier distribution between the interfaces is changed considerably [20)]. For the emulsion polymerization of styrene with SDS and KPS it was shown that the influence of R_{pm} with respect to the emulsifier distribution cannot be neglected at low emulsifier concentrations [11)]. In the case of surfactant-free polymerizations it was shown that a control of the hydrodynamic conditions (stirrer speed and stirrer geometry) is important for the reproducibility with respect to particle size and particle size distribution [21)]. In large scale technical reactors it is much more necessary to attach importance to the hydrodynamic conditions than in labscale reactors. If the stirring conditions are not optimized problems can arise regarding the homogeneity of the reaction mixture as well as the heat removal in the case of insufficient mixing. In contrast, if the shear forces are too high the latex may become unstable with respect to coagulation [22)]. Most of the investigations have been carried out by increasing the stirrer speed starting from well mixed conditions [20, 22)]. Additional to these results the data depicted in Figures 4 and 5 prove an influence of the stirrer speed also at emulsifier concentrations well above the critical micelle concentration and also at much lower stirrer speeds. The lower stirrer speeds are so low that a bulky free monomer phase is formed on top of the reaction mixture. This seems to be crucial as under these conditions the monomer diffusion is effectively hindered compared to higher stirrer speeds where monomer droplets are present.

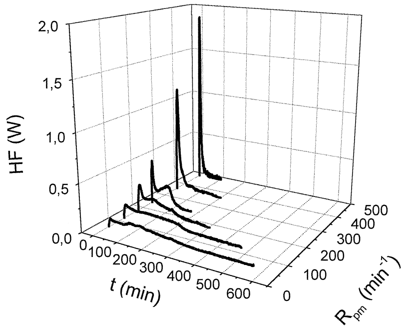

Fig. 4 Change of the heat flow (HF) in dependence on R_{pm} [17)]

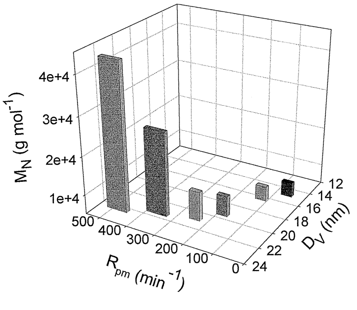

Fig. 5 Change of M_N and D_V in dependence on R_{pm} [17)]

To verify these results polymerizations have been repeated in all glass reactors with SDS and an alkylsulfonate (E30) as surfactant, respectively [23)]. In contrast to the calorimeter experiments the reaction volume was doubled, the stirrer type was changed, and hence, the hydrodynamic conditions were completely altered. However, the results confirm the calorimeter experiments. The lower the stirrer speed the lower both the average particle size and the average molecular weight (cf. Table 5). The latexes prepared with the low stirrer speed have D_V values less than 10 nm but a broad particle size distribution. This is for polystyrene latexes remarkably small. However, TEM pictures (Fig. 6) of dialyzed samples confirm the presence of particles in the range between 30 nm down to 5 nm or even smaller still and reveal that these latexes are stable to coagulation even if a part of the surfactant is replaced by dialysis.

Table 5. Influence of the stirrer speed on latex and polymer properties

Run	D_V (nm)	M_W (g mol^{-1})	M_N (g mol^{-1})
E30-S	$19{,}5 \pm 4{,}4$	$1{,}0\cdot10^{5} \pm 3{,}2\cdot10^{4}$	$4{,}2\cdot10^{4} \pm 9{,}1\cdot10^{3}$
E30-L	$8{,}5 \pm 1{,}0$	$9{,}9\cdot10^{3} \pm 2{,}3\cdot10^{3}$	$4{,}1\cdot10^{3} \pm 1{,}5\cdot10^{3}$
SDS-S	$19{,}0 \pm 1{,}7$	$1{,}3\cdot10^{5} \pm 1{,}4\cdot10^{4}$	$5{,}0\cdot10^{4} \pm 8{,}7\cdot10^{3}$
SDS-L	$9{,}1 \pm 3{,}0$	$8{,}4\cdot10^{3} \pm 1{,}0\cdot10^{3}$	$3{,}7\cdot10^{3} \pm 1{,}5\cdot10^{3}$

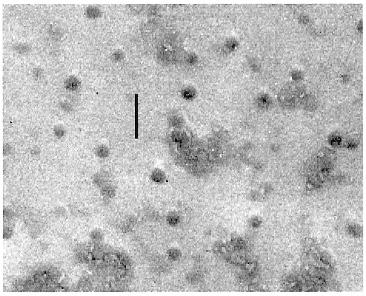

Fig. 6a TEM picture of a calorimeter latex;stirrer speed 60 rpm; bar indicates 100 nm

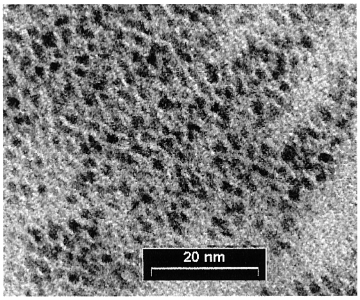

Fig. 6b TEM picture of a glass reactor latex; stirrer speed 50 rpm

A satisfying explanation of this effect is alas not possible at the moment. It is very likely that the reduced stirrer speed has an influence on the monomer diffusion into the aqueous phase and after nucleation also into the latex particles. A lower monomer concentration leads to lower molecular weights (cf. Table 5) and also to a smaller particle growth. But a direct connection to particle nucleation is not obvious. However, it had been also observed in semi-batch vinyl chloride emulsion polymerizations that with decreasing monomer reservoir temperature (which means an increasing monomer starvation) the average particle size had been decreased to less than 5 nm 24).

In conclusion, experimental as well as theoretical investigations of particle nucleation in *ab initio* emulsion polymerization are a challenging task. Classical approaches have to be modified or to be left if more and more results of new experimental investigations are to be known. The experimental fact that surfactants under special circumstances can prevent nucleation as well as the strong influence of the reactor material and of the electrolyte concentration on nucleation are examples which can at least qualitatively be explained within the frame of the classical nucleation theory. On the other hand an even qualitative explanation of the strong influence of the stirrer speed on nucleation needs more experimental and theoretical investigations.

Acknowledgment

The authors wish to thank Mrs. R. Rafler and Mrs. S. Pirok for preparative and analytical assistance. Financial support from the Max Planck Society is gratefully acknowledged.

References

1. K. Tauer, I. Kühn, in J. M. Asua (ed.) *Polymeric Dispersions: Principles and Applications*, Kluwer Academic Publishers, Dordrecht, Boston, London 1997, p.49
2. K. Tauer, R. Deckwer, I. Kühn, C. Schellenberg, Coll. Polym. Sci., in press
3. R. G. Gilbert, Emulsion Polymerization - A Mechanistic Approach, Academic Press, London, San Diego, New York, Boston, Sydney, Tokyo, Toronto, 1995, p.305
4. A. Laaksonen, V. Talanquer, D. W. Oxtoby, Ann. Rev. Phys. Chem. **46**, 489 (1995)
5. The polymerizations were carried out batchwise at 60 °C in a sealed test tube of different materials in 10 ml of water. The starting reaction mixture was homogeneous consisting of dissolved MMA or styrene, different amounts of emulsifier ranging from zero up to concentrations well above the critical micelle concentration, and initiator. Different emulsifier – initiator combinations were investigated: sodium lauryl sulfate (SDS), cetyl trimethyl ammonium bromide (CTAB), and IGEPAL CO 880 as emulsifiers and 2,2'-azobis(2-amidinopropane)dihydrochloride (V50), KPS, and a poly(ethylene glycol)-azo-initiator (PEGA200) as initiators. The filled test tubes were placed for 2 hours in a water bath whose temperature was adjusted so that inside the test tubes 60 °C was reached. All runs were repeated in 10 different test tubes in order to investigate the reproducibility and to get representative data. After the polymerizations the latexes were characterized with respect to average particle size D_V (volume

weighted average particle size from dynamic light scattering (DLS) with a Nicomp particle sizer) and molecular weight distribution (GPC in THF with polystyrene standards). Transmission electron microscopy (TEM) was performed on a Zeiss EM 912 Omega.

J. H. Baxendale, M.G. Evams, G.S. Park, *Trans. Faraday. Soc.* **42**, 155 (1946)

J. H. Baxendale, M.G. Evams, G.S. Park, *Trans. Faraday Soc.* **42,** 668 (1946)

V.J. Frilette, W.P. Hohenstein, *J. Polym. Sci.* **III,** 22 (1948)

F. A. Bovey, I. M. Kolthoff, *J. Polym. Sci.* **V** 487 (1950)

R. M. Fitch, M. B. Prenosil, K. J. Sprick, *J. Polym. Sci.* **C 27,** 95 (1969)

R. M. Fitch, C. Tsai, *Polymer Letters* **8**, 703 (1970)

F. Wenzel, K. Lehmann, *Ullmann Lexikon der Technischen Chemie*, 4. Edition, VCH Weinheim volume 16, 1978, p.610

J. Lane, *Ind. Eng. Chem., Anal. Ed.* **18**, 295 (1946)

If $D_V = 0$ it was impossible to detect particles with the DLS equipment used. It was concluded that no particles have been formed.

W. J. Lyman *Solubility in Water* in *Handbook of Chemical Property Estimation Methods*, W. J. Lyman, W. F. Rehl, D. H. Rosenblatt (eds.), ACS Washington, 1990

R. G. Gilbert, Emulsion Polymerization - A Mechanistic Approach, Academic Press, London, San Diego, New York, Boston, Sydney, Tokyo, Toronto, 1995, p.337

The polymerizations were carried out batchwise in a reaction calorimeter (RM200S calorimeter ChemiSens AB, Lund, Sweden) which consists of glass walls and both a stainless steel bottom and stirrer. 13,9 mM SDS), 115,2 mM styrene monomer, and 5,9 mM KPS were polymerized at different stirrer speeds at 70 °C. R_{pm} was varied between 60 min^{-1} and 480 min^{-1}. At the lowest stirrer speed a bulky free monomer phase was formed on top of the reaction mixture.

H. Gerrens, Fortschr. Hochpol. Forsch. **1**, 234 (1959)

K Arai, M Arai, S Iwasaki, S Saito. J. Polym. Sci. Polym. Chem. Ed. **19**, 1203 (1981)

M. Nomura, M. Harada, W. Eguchi, S. Nagata, *J. Appl. Polym. Sci.* **16**, 835 (1972)

J. W. Goodwin, J. Hearn, C. C. Ho, R. H. Ottewill, Coll. Pol. Sci. **252**, 464 (1974)

T. R. Aslamazova Coll. J. **61**, 139 (1999)

The polymerizations were carried out batchwise in a 250 ml all-glass reactor. 12,2 mM E30 a sodium alkylsulfonate with an average carbon chain length of C_{15} or 13,9 mM SDS were used as surfactants, 115,2 mM styrene monomer, and 5,9 mM KPS were polymerized at different stirrer speeds at 70 °C. The stirrer speed was either 50 or 350 revolutions per minute. At a stirrer speed of 50 rpm the monomer formed a bulky phase on top of the reaction mixture. In order to determine the reproducibility each experiment was repeated six times. E30-L, SDS-L and E30-S, SDS-S refer to the slow and the fast stirrer speed in the presence of SDS and E30, respectively. For TEM photographs the samples were sputtered with platinum to enhance the contrast.

K. H. Goebel, H. J. Schneider, W. Jaeger, G. Reinisch, *Acta Polymerica* **33,** 49 (1982)