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ORIGINAL CONTRIBUTION

A. Kampes
B. Tieke

Emulsifier-free emulsion polymerization of the comonomer system styrene/tetrahydrofurfuryl methacrylate

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A. Kampes · B. Tieke (✉)
Institut für Physikalische Chemie
der Universität zu Köln
Luxemburger Straße 116
50939 Köln

Abstract The emulsifier-free emulsion copolymerization of styrene and tetrahydrofurfuryl methacrylate (TMA) in aqueous phase is described. Monodisperse latex particles with diameters from about 280 to 620 nm are obtained consisting of a hydrophobic polystyrene core and a hydrophilic poly-TMA shell. The influence of a variation of TMA, styrene and initiator (potassium persulfate) concentration in the original emulsion on particle size, molecular weight and composition of the copolymer is described. The concentration of TMA and initiator affects the number of primary particles but not the size of the final particles, whereas the styrene concentration strongly influences the particle diameter, a large size being favored by a high styrene concentration. The molecular weights of the polymers are between 6.2×10^4 and 7.0×10^5 g/mole. Size exclusion chromatography of polymer solutions in tetrahydrofuran shows that high molecular weights are especially found in large particles, which are preferentially formed in emulsions with a high concentration of styrene. ^{1}H-NMR spectroscopy of the polymer shows that only about 50% of the initial TMA concentration are polymerized in the particles. Thus the copolymers prepared at increasing styrene concentration and constant initiator concentration of the emulsion show an increasing polystyrene content and are formed in particles of increasing size.

Key words Functionalized latex particles – emulsion polymerization – styrene – tetrahydrofurfuryl methacrylate

Introduction

The emulsifier-free emulsion polymerization has been proven to be a suitable method for the preparation of monodisperse polymer particles. Use of hydrophilic and hydrophobic comonomers allows to prepare core-shell latex particles with hydrophobic core and hydrophilic shell. Suitable comonomers are styrene as the hydrophobic compound and acrylic acid, methacrylic acid, itaconic acid and fumaric acid [1, 2]; sodium styrenesulfonate and sodium 2-sulfoethyl methacrylate [3], sodium undecylisothionate, sodium methallylsulfonate [4, 5], 1,2-dimethyl 5-vinylpyridinium methylsulfate and 1-ethyl 2-methyl 5-vinylpyridinium bromide [6], 4-vinylpyridine [7] and 4-vinylbenzylamine hydrochloride [8] as ionic hydrophilic compound. Particles have also been prepared from styrene and nonionic hydrophilic comonomers such as 2-hydroxyethyl methacrylate [9, 10], acrylamide [11, 12] and derivatives [13] or 2,3-epoxyethyl methacrylate [14]. Mechanistic studies on particle nucleation and growth as well as studies on the relation between reaction conditions

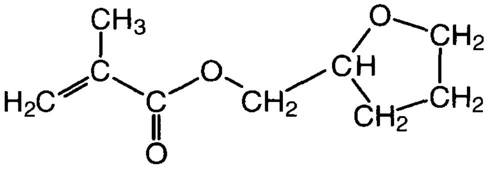


Fig. 1 Structure of the hydrophilic comonomer tetrahydrofurfuryl methacrylate

and particle and copolymer properties were mainly carried out on systems based on styrene and ionic comonomers [3, 6, 7]. However, nonionic hydrophilic comonomers form copolymers with styrene, which are usually much better soluble in common organic solvents such as tetrahydrofuran (THF), for example, and therefore, can be analyzed more easily on their comonomer composition, molecular weight and weight distribution.

In order to get more information on the factors determining the formation of particles with nonionic shell, we decided to study new core-shell latex particles based on styrene and tetrahydrofurfuryl methacrylate (TMA, Fig. 1). Influences of comonomer ratio, monomer and initiator concentration on particle size, molecular weight and composition of the copolymer are reported. Analytical methods used in this study comprise the particle size determination by scanning electron microscopy (SEM), the determination of molecular weight and weight determination using size exclusion chromatography (SEC) and the determination of the copolymer composition using ^{1}H-NMR spectroscopy.

Additional interest on these particles arises from the high concentration of THF-moieties in the shell making the particles interesting as nonvolatile, polymer-bound solvent, easy to recover and thus potentially useful in replacing the moderately hazardous solvent THF in organic syntheses [15, 16].

Experimental section

Materials

Styrene (industrial grade, Aldrich) was purified by vacuum destillation and used as a monomer together with tetrahydrofurfuryl methacrylate (TMA) from Sartomer (West Chester, PA 19382, USA), which was used without further purification. Potassium persulfate (KPS) was recrystallized from acified water. Nitrogen used for preparation of the particles was purged from oxygen, water and CO_2 using a BTS^{TM} catalyst (Cu_2O), concentrated sulfuric acid and bulk potassium hydroxide, respectively. The ionic strength was 7.41×10^{-3} moles l^{-1} for investigations with constant initiator concentration. For the experiments with variable initiator concentration, the ionic strength was adjusted to 3.99×10^{-2} moles l^{-1} by adding sodium sulfate.

Preparation of the particles

A 500 ml three-necked flask equipped with stirrer, condenser and gas inlet was used. 280 ml of water were filled into the flask, heated to 70 °C and purged with nitrogen for 30 min. Under nitrogen atmosphere, first the TMA and then the styrene were filled into the flask. After further purging with nitrogen for 10 min potassium persulfate dissolved in 20 ml of water was added. The amounts of styrene, TMA and initiator used in the various experiments are listed in Table 1. In case of a variation of the styrene content, the total reaction volume was always kept constant at 400 ml, i.e. with increasing styrene concentration the water content was reduced accordingly. In the experiments with variable initiator concentration, potassium persulfate was successively replaced by sodium sulfate to keep the ionic strength constant. After addition of all compounds, the gas inlet was removed and the reactor was closed. Already a few minutes later the solution became turbid until finally a white and milky dispersion was obtained. After 18 h the reaction was stopped by adding 150 ml of methanol and cooling to room temperature. The particles were separated by filtration of the emulsion through glass wool to remove aggregated material and subsequent centrifugation at 3000 rpm for 4–6 h. For purification, the particles were fourfold redispersed in a methanol/water mixture and separated by centrifugation. In each redispersion/centrifugation cycle the amount of methanol in the methanol/water mixture was increased until finally pure methanol was used. Then the particles were dried to constant weight in a vacuum drier at 40 °C for about two days. 40–70 wt% of the theoretical yield were obtained (10% were lost as coagulated particles during filtration and the residual part remained in the liquid phase after centrifugation).

Methods

For determination of the particle diameter, a scanning electron microscope (Philips SEM 515) was used. Samples were prepared by dropping particle dispersions in ethanol onto polished aluminium plates and drying in vacuum at 40 °C. Particle sizes were determined by evaluating 100 particles from the photographs using a scaled magnifying lens. The mean error was about two percent. Weight and number average of the particle diameter, D_w and D_n, were

Table 1 Effects of different TMA, KPS and styrene concentration in original reaction mixture on number and weight average of molecular weight and particle diameter as well as polydispersity of particle size

Sample no.	TMA[1] [10^{-2} mole]	Styrene [mole]	KPS[2] [10^{-4} mole]	NA_2SO_4 [g]	M_w	M_n [10^5 g/mol]	D_w [nm]	D_n [nm]	D_w/D_n[3]
1	0.401	0.260	7.40	—	6.18	1.34	568 ± 11	509 ± 11	1.116
2	0.802	0.260	7.40	—	7.03	1.19	488 ± 10	476 ± 10	1.025
3	1.200	0.260	7.40	—	2.50	0.41	401 ± 9	395 ± 9	1.015
4	1.610	0.260	7.40	—	1.80	0.74	385 ± 9	384 ± 9	1.003
5	0.401	0.260	2.52	0.531	3.07	1.28	418 ± 10	412 ± 10	1.015
6	0.401	0.260	5.07	0.496	5.30	3.40	552 ± 11	524 ± 11	1.053
7	0.401	0.260	7.40	0.462	3.74	0.69	617 ± 11	599 ± 11	1.030
8	0.401	0.260	17.7	0.317	2.33	0.48	439 ± 10	412 ± 10	1.066
9	0.401	0.260	40.0	—	1.27	0.28	313 ± 9	304 ± 9	1.030
10	1.610	0.087	7.40	—	0.62	0.17	285 ± 8	285 ± 8	1.000
11	1.610	0.175	7.40	—	1.34	0.33	363 ± 9	363 ± 9	1.000
12	1.610	0.350	7.40	—	4.31	0.69	505 ± 11	504 ± 11	1.000
13	1.610	0.437	7.40	—	4.93	0.90	548 ± 11	547 ± 11	1.000
14	1.610	0.524	7.40	—	5.11	0.89	526 ± 11	525 ± 11	1.000
15	1.610	0.699	7.40	—	4.80	1.04	495 ± 10	488 ± 10	1.031

[1] Tetrahydrofurfuryl methacrylate.
[2] Potassium persulfate.
[3] Polydispersity.

calculated from

$$D_w = \frac{\sum N_i \cdot D_i^4}{\sum N_i \cdot D_i^3} \quad \text{and} \quad D_n = \frac{\sum N_i \cdot D_i}{\sum N_i},$$

where N_i denotes the number of particles with diameter D_i. The polydispersity is given by the quotient of D_w and D_n.

Molecular weight and weight distribution were determined using a size exclusion chromatography from Waters/Millipor. A combination of Latek–Styragel columns with pore sizes of 50, 100 and 1000 nm was used. The fluid phase was tetrahydrofuran (THF) with a flow rate of 1 ml min^{-1}. A UV-detector working at $\lambda = 254$ nm was used. Some samples were also analysed with an RI detector. NMR spectra were taken on an AC 300 spectrometer from Bruker. The solvent was $CDCl_3$ containing TMS as an internal standard.

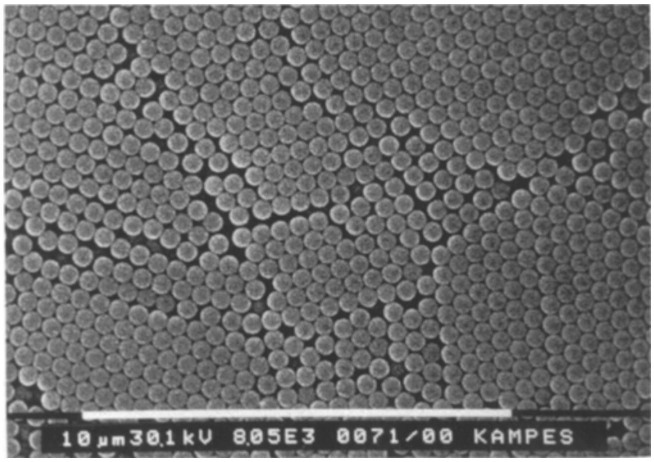


Fig. 2 SEM micrograph of polystyrene/poly-TMA particles

Results and discussion

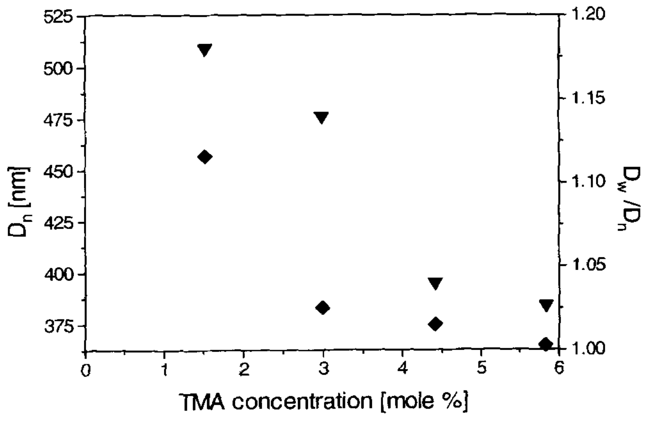
The emulsifier-free emulsion copolymerization of styrene and TMA typically leads to monodisperse particles with diameters from 300 to 600 nm. In Fig. 2, a scanning electron micrograph of the particles is shown, which indicates the narrow size distribution.

In the following the influences of the preparation conditions on the particle properties are described. The discussion takes into account the rather complex mechanism of emulsifier-free emulsion polymerization in presence of water-soluble monomers derived from previous investigations [3, 6, 7]. According to this mechanism, polymerization starts in the aqueous phase and involves the water soluble hydrophilic monomer and the few dissolved hydrophobic styrene molecules. With increasing length, the growing polymer chains gradually attain amphiphilic properties, which in their extent are depending on the relative concentration of the monomers and their reactivity in copolymerization. The increasing hydrophobicity of the growing chains leads to nucleation of precursor particles, which aggregate to mature particles. These particles are stabilized by the hydrophilic parts of the growing chains. As soon as the particles are formed, styrene is transformed from the droplets into the hydrophobic core of the particles and causes that polymerization mainly takes place within the core of the particles. In addition, water-soluble polymer may be formed due to termination reactions in the aqueous phase and styrene depletion in water at high conversion. According to this mechanism, the number of particles is determined in the aggregation process and remains essentially constant throughout the residual part of the reaction.

Effect of TMA concentration on particle size and molecular weight of the copolymer

In a first series of experiments, styrene and initiator concentration were kept constant and the TMA concentration was varied. The reaction was initiated with 0.28 mol% of KPS. As shown in Fig. 3, the number average of the particle diameter D_n, as well as the polydispersity D_w/D_n, decrease with increasing TMA concentration. On increasing the TMA concentration from about 1.5–6 mol%, the polydispersity changes from 1.12 to nearly one and the particle size drops from 509 nm to about 380 nm. The detailed data are compiled in Table 1 (samples 1–4). The decrease of the particle size is in accordance with the literature [10, 14] and originates from the fact that a higher concentration of hydrophilic comonomer leads to more growing polymer chains, which aggregate to a higher number of primary particles. As a consequence, less styrene is available for polymerization in each particle and thus the resulting particles must be of smaller size. The decrease in polydispersity has its origin in the larger number of primary particles at higher TMA concentration so that deviations from the average size become increasingly less significant.

Fig. 3 Plot of the particle diameter D_n (▼) and the polydispersity D_w/D_n (◆) versus the TMA concentration in the original reaction mixture



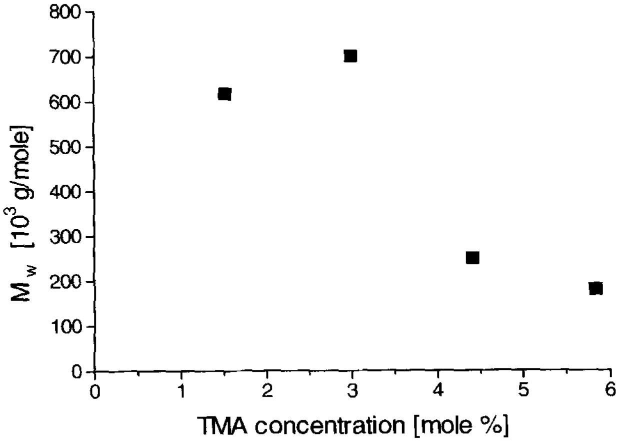


Fig. 4 Plot of the molecular weight M_w of the resulting copolymer versus the TMA concentration in the original reaction mixture

To study the molecular weight, the resulting particles were dissolved in THF and the polymer analyzed by size exclusion chromatography (SEC). Elution curves obtained by UV and RI detection were always nearly identical, indicating that all copolymer fractions are rich in polystyrene. This means that TMA rich copolymer fractions only recognizable with the RI detector can only be present in negligible concentration. Number and weight average of the molecular weights, M_n and M_w, are listed in Table 1 (samples 1–4). In Fig. 4, M_w is plotted versus the TMA concentration in the original reaction mixture. Despite of a large scatter of the M_w data, it can be recognized that the molecular weights are decreasing when the amount of TMA in the reaction mixture is increased. This is reasonable because with increasing TMA concentration a larger number of primary particles is formed, which contain less styrene per particle since the overall concentration of styrene in the system is constant. Consequently, polymerization already terminates at a shorter chain length.

Effect of initiator concentration on particle size and molecular weight of the copolymer

In a second set of experiments, the initiator concentration was varied and the effect on the molecular weight of the polymer and the size of the particles was investigated. These experiments were carried out at a constant styrene:TMA molar ratio of 66:1. The resulting particle size and molecular weight of the polymer are listed in Table 1 (samples 5–9). In Fig. 5, the weight average of the molecular weight, M_w, is plotted versus the KPS concentration (in mole percent of total monomer concentration)

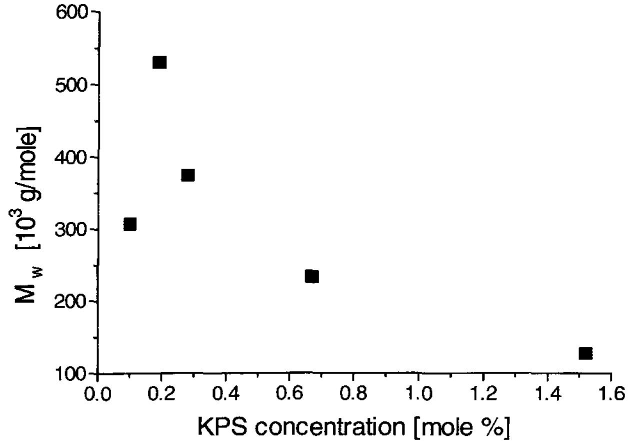


Fig. 5 Plot of the molecular weight M_w of the resulting copolymer versus the initiator (KPS) concentration (in mol% of total monomer concentration) in the original reaction mixture

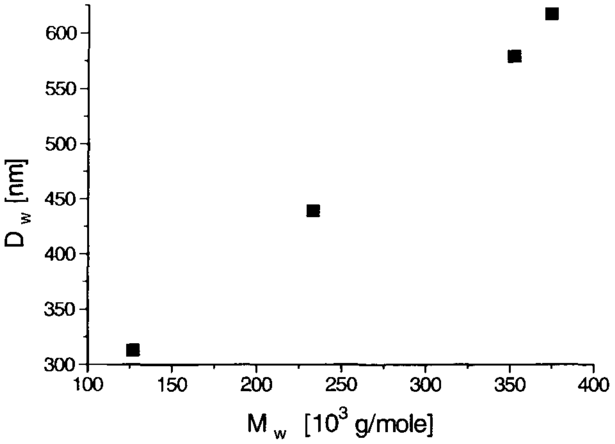


Fig. 7 Plot of particle diameter D_w versus the molecular weight of copolymer M_w

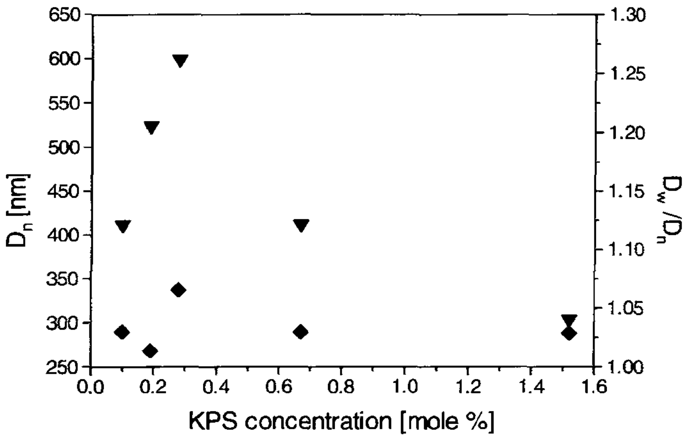


Fig. 6 Plot of the particle diameter D_n (▼) and the polydispersity D_w/D_n (◆) versus the initiator (KPS) concentration (in mol% of total monomer concentration) in the original reaction mixture

in the original reaction mixture. At very low initiator concentration, an increase of the amount of KPS leads to higher molecular weights. The reason is that the number of growing chain ends increases so that termination reactions originating from impurities become less important. If the KPS concentration exceeds 0.2 mol%, the molecular weight decreases again. The origin is that at higher KPS concentration more chains are initiated, which at a certain conversion aggregate to a larger number of particles. Since the styrene concentration remains constant, increasingly less styrene is available for each particle and shorter polymer chains are formed. In Fig. 6, particle diameter and polydispersity are plotted versus the KPS concentration. The polydispersity of the particles is nearly one and does not significantly vary with the KPS concentration. The particle diameter nearly shows the same dependence on the initiator concentration as the molecular weight of the polymer. Only the position of the maximum is slightly different. Obviously, the reasons for obtaining a high molecular weight are basically the same as for getting large particles. Hence, there should be a linear relation between the particle diameter and the molecular weight of the polymer. As shown in Fig. 7, this is in fact the case.

In case of the highest KPS concentration of 1.52 mol%, initiator and hydrophilic comonomer have reached equal concentration in the original reaction mixture. Since the polymerization proceeds for about 18 h and the half-life of KPS is only 3 h at the reaction temperature of 70 °C [17], it can be expected that the number of initiated chains has reached a maximum value and a further increase of the initiator concentration does not affect the number of primary particles anymore. As a consequence, the lower limit of particle size has been reached and even smaller particles cannot be prepared.

Effect of styrene concentration on particle size and molecular weight of the copolymer

In the third set of experiments, the amount of TMA and initiator was kept constant at 1.61×10^{-2} and 7.40×10^{-4} mole, respectively, while the amount of styrene was varied and the effect on molecular weight and particle size was studied. Details of the experimental conditions are listed in Table 1 (samples 4, 10–15) together with the particle size and the molecular weight of the copolymer. As can be seen from the plots of Figs. 8 and 9, the molecular

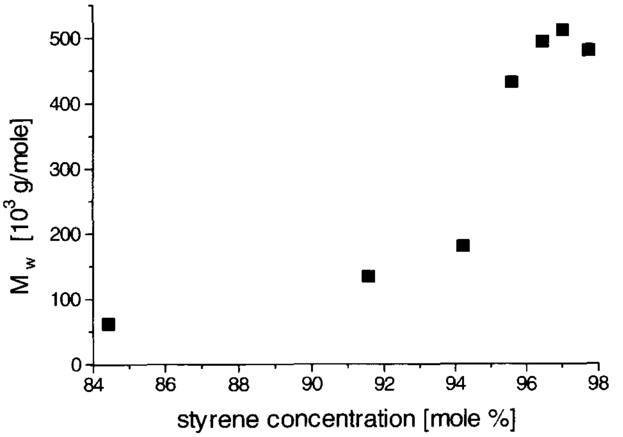


Fig. 8 Plot of molecular weight M_w versus the concentration of hydrophobic comonomer styrene in the original reaction mixture

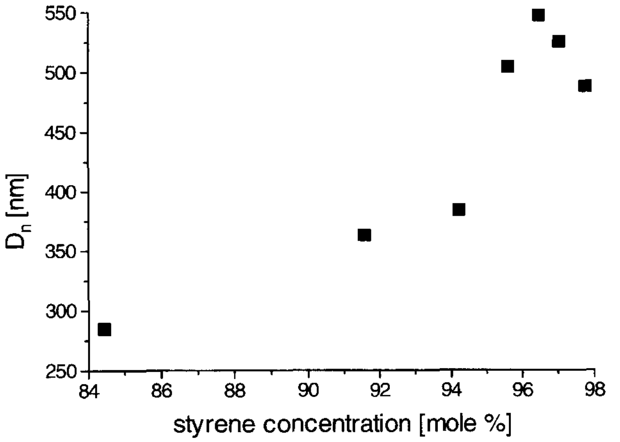


Fig. 9 Plot of particle diameter D_n versus the concentration of hydrophobic comonomer styrene in the original reaction mixture

weight, M_w, and the particle diameter, D_n, increase with the amount of styrene added to the reaction mixture. The origin is easily explained: The number of primary particles is independent from the styrene concentration, but the amount of styrene available for the individual particles increases. Consequently, the particles grow and the polymer chains become much longer. If at the present initiator concentration a styrene:TMA molar ratio of 28:1 is exceeded, molecular weight and particle size have reached maximum values of 500.000 and 530 nm, respectively. The reason could be that under the reaction conditions the initiator concentration is not sufficient to polymerize the residual monomeric styrene. Hence, the surplus addition of styrene leads to larger and larger particles, but the styrene in the particles remains unpolymerized and is leached out during the successive working up procedure. As a result, polymer particles of constant size are obtained.

Relation between copolymer composition and comonomer ratio of the starting reaction mixture

As the styrene/TMA copolymer from the particles is well soluble in organic solvents such as $CDCl_3$, its composition can be determined by ^{1}H-NMR spectroscopy. The signals of the five aromatic protons in the styrene unit and the five aliphatic protons in the $-CH_2-O-$ and $>CH-O-$ groups of TMA were evaluated. The ratio of the peak areas is a direct measure of the copolymer composition. In Table 2 (upper part), the integrated peak areas and the calculated copolymer compositions are listed for samples with three comonomer concentrations in the starting mixture. It turns out that the hydrophilic TMA is only partly incorporated in the particles. Though only few data are available at present, it can be concluded that about 50% of the original TMA is polymerized in the particles independent of the absolute concentration in the starting reaction mixture. The whereabouts of the residual TMA are not quite clear yet. ^{1}H-NMR spectra of the aqueous (D_2O) phase subsequent to removal of the polymerized particles do not show any residual TMA. Either homopolymerization of TMA in solution is possible followed by polymer adsorption at the particle surface and subsequent desorption during the purification steps or, alternatively, monomer is adsorbed at the particle surface and subsequently desorbed during the purification procedure. Comparing the TMA concentration in the copolymer listed in Table 2 with the particle size listed in Table 1, an inverse relationship is found. The reason is that after the particle nucleation the further growth is only due to styrene

Table 2 Copolymer composition of samples prepared from different TMA and KPS concentration in starting reaction mixture[1]

Sample no.	Peak area in arb. units[2]		TMA in copolymer [mol%][3]
	Styrene	TMA	
2	932.9	11.9	1.26
3	555.1	13.9	2.44
4	567.2	19.0	3.24
5	876.6	12.1	1.36
6	430.4	2.3	0.53
7	852.2	7.0	0.82
8	488.1	3.9	0.79

[1] For TMA and KPS concentration see Table 1.
[2] As determined by ^{1}H-NMR spectroscopy.
[3] Mol% of total monomer concentration.

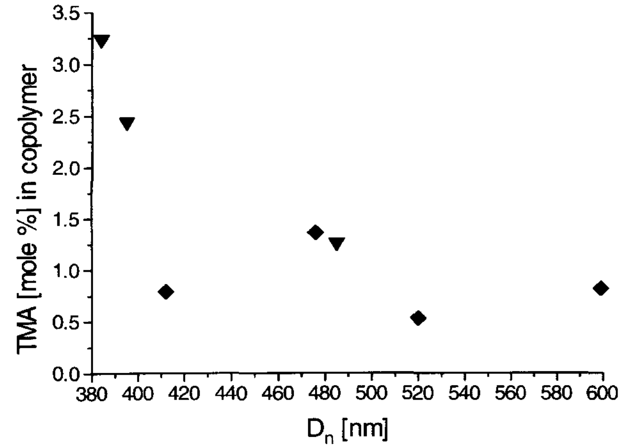


Fig. 10 Plot of TMA concentration in copolymer versus particle size D_n for samples prepared at different TMA monomer concentration (◆) and at different KPS concentration (▼) in the original reaction mixture

polymerization in the core of the particles. Therefore, a high styrene concentration in the starting mixture leads to large particles consisting of a copolymer with a high polystyrene content.

In a further set of experiments, the influence of the initiator concentration on the copolymer composition was studied. Again, the composition of the copolymer was analyzed using ^{1}H-NMR spectroscopy. In Table 2 (lower part), integrated areas of polystyrene and poly-TMA signals are listed together with the calculated TMA concentration of the copolymer. It turns out that there is no clear effect of the initiator concentration on the copolymer composition. For all samples, only about half of the initial TMA concentration is present in the copolymer, no matter what the original initiator concentration was. The reason is that both a low and a high initiator concentration favor a high TMA content of the copolymer. At low initiator concentration, early chain termination is favored by impurities. Since TMA is preferentially polymerized in the early stage of the reaction, the TMA content of the resulting copolymer must be high. At high initiator concentration, a large number of particles is formed so that at constant styrene concentration the amount of styrene available for the individual particles is diminished. Again, the TMA content of the copolymer must be high. In Fig. 10, the copolymer compositions listed in Table 2 are plotted versus the particle sizes of the individual samples with different initiator and TMA concentration derived from Table 1. It can be seen that the polymer particles prepared at constant comonomer ratio but different initiator concentration exhibit nearly the same copolymer composition although the particle size is significantly different, while particles prepared at different comonomer ratio and constant initiator concentration show a decreasing TMA concentration in the copolymer when the particle size increases.

Conclusions

Our study shows that tetrahydrofurfuryl methacrylate is a useful monomer to prepare nonionic monodisperse latex particles by soap-free emulsion copolymerization with styrene. New particles with a high concentration of tetrahydrofuran groups in the shell are obtained, whose materials properties are presently under investigation. Because of their hydrophilicity, the tetrahydrofuran groups are most likely situated in the shell although a definite proof is still lacking at present. No indications were found that the course of the polymerization deviates significantly from the established mechanism of emulsifier-free emulsion copolymerization of styrene with ionic monomers. Our study indicates that parameters such as hydrophilic comonomer and initiator concentration strongly affect the number of primary particles, but are not important for the final size of the (co)polymerized particles. The final size depends on the amount of styrene available for each of the growing particles and the number of growing chain ends therein. This may explain that different research groups observe the same tendencies although the particular systems are quite different [6, 8]. High molecular weights are especially found in large particles, i.e. in particles polymerized at a high concentration of styrene in the original emulsion.

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References

1. Ceska GW (1974) J Appl Polym Sci 18:427–437
2. Sakota K, Okaya T (1976) J Appl Polym Sci 20:3265–3274
3. Juang MSD, Krieger IM (1976) J Polym Sci, Polym Chem Ed 14:2089–2107
4. Chen SA, Chang HS (1985) J Polym Sci, Polym Chem Ed 23:2615–2630
5. Chang HS, Chen SA (1988) J Polym Sci, Polym Chem Ed 26:1207–1229
6. Liu LJ, Krieger IM (1981) J Polym Sci, Polym Chem Ed 19:3013–3026

7. Ohtsuka Y, Kawaguchi H, Hayashi S (1981) Polymer 22:658–662
8. Delair T, Marguet V, Pichot C, Mandrand B (1994) Coll Polym Sci 272: 962–970
9. Kamei S, Okubo M, Matsumoto T (1986) J Polym Sci, Polym Chem Ed 24:3109–3116
10. Chen SA, Chang HS (1990) J Polym Sci, Polym Chem Ed 28:2547–2561
11. Ohtsuka Y, Kawaguchi H, Sugi Y (1981) J Appl Polym Sci 26:1637–1647
12. Chen SA, Lee ST (1991) Macromolecules 24:3340–3351
13. Kawaguchi H, Sugi Y, Ohtsuka Y (1981) J Appl Polym Sci 26:1649–1657
14. Zurkova E, Bouchal K, Zdenkova D, Pelzbauer Z, Svec F, Kalal J, Batz HG (1983) J Polym Sci, Polym Chem Ed 21:2949–2960
15. Molnar LK, Buchwald SL, Hatton TA (1996) ACS Polymer Prepr 36:113–114
16. Anastas PT, Ferris CA (eds) (1994) In: Benign by Design: Alternative Synthetic Design for Pollution Prevention. ACS, Washington DC, pp 2–23
17. Kolthoff IM, Müller IK (1951) J Am Chem Soc 73:3055–3059