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ORIGINAL CONTRIBUTION

Synthesis of styrene–butadiene rubber latex via miniemulsion copolymerization

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Abstract High-butadiene-level styrene–butadiene rubber latexes up to high solid-contents are synthesized using the miniemulsion process. It is shown that the miniemulsion polymerization approach offers an efficient heterophase route synthesizing styrene–butadiene copolymer latexes with flexible copolymer composition and narrow size distribution of the resulting latex particles. Secondary nucleation was successfully prevented by using a hydrophobic initiator. Due to the nanoreactor situation, even at high conversions, a low crosslinking degree and, therefore, low gel contents are obtained. The microstructure of the polymers obtained in miniemulsion is independent of the synthesis parameters, especially the temperature. The molecular weight can be easily adjusted by the application of transfer agents while the insoluble gel content is substantially reduced. An up-scaling of the procedure is easily possible.

Keywords Miniemulsion · Butadiene · Copolymers · Latex

Introduction

The homopolymer polybutadiene (PB) and copolymers consisting of butadiene and styrene are some of the most relevant technical rubbers. They can be synthesized radically or anionically in solution or industrially in most cases by heterophase polymerization, mostly emulsion polymerization. The type and condition of polymerization determine the resulting microstructures of the polymers. Anionic polymerization of butadiene using *n*-butyl or *sec*-butyl lithium as initiator leads typically to microstructures with a composition of 35% 1,4 cis, 55% 1,4 trans, and 10% 1,2 units. However, PB and styrene–butadiene rubber (SBR) latexes are usually produced via typical radical emulsion polymerization processes. Here, two major processes differing in reaction temperature are employed ("cold rubber" and "hot rubber" process). The "cold rubber" polymerization is performed at 5 °C using redox initiator systems. A chain transfer agent, such as a mercaptane, is added to control the molecular weight distribution; therefore, the typically high molecular weights in emulsion polymerization can be suppressed. For "hot rubber" polymerization, potassium persulfate is the most commonly used initiator at temperatures of about 70 °C. The microstructure composition of "cold" and "hot rubber" SBR latexes (with 23.5% styrene) is usually described as a statistical copolymer. "Cold rubber" typically displays a microstructure in the butadiene component of approximately 9% 1,4 cis, 54.5% 1,4 trans, and 13% of the vinylic isomer, whereas the "hot rubber" exhibits a higher amount of 1,4 cis units, i.e., 15% [1, 2]. At high conversion, a crosslinking of the polymer chains is observed. Therefore, especially in industrial application, the polymerization is usually performed only up to 70% conversion.

For materials application, SBR polymer latexes with high trans fractions, low crosslinking degrees, and high butadiene contents are desired. These characteristics should be obtained at high reaction temperatures so that expensive cooling of the system can be avoided.

A highly versatile and flexible methodology for the preparation of polymer latexes is displayed by the miniemulsion process [3]. This technique was already reported

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as a suitable method to synthesize styrene–butadiene copolymer latexes; however, the butadiene content was only 30% in this case [4]. The gel fraction, which is coupled to the crosslinking degree, is reported to be reduced by the miniemulsion approach compared to emulsion polymerization. The gel fraction at high conversions of polymer produced via the miniemulsion technique was considerably lower (70 wt.%) than in conventional emulsion polymerization, where high conversion results in high gel fraction (>90%) [5]. However, high styrene-containing SBR latexes are of minor industrial interest compared to the high butadiene-containing latexes with a butadiene to styrene ratio of 76.5:23.5.

Keeping this in mind, we focused on the realization of high-butadiene-levels SBR latexes up to high solid contents using the miniemulsion process. We will show that the miniemulsion polymerization approach offers an efficient heterophase route synthesizing a styrene–butadiene copolymer latex with flexible copolymer composition and narrow size distribution of the resulting latex particles. Instead of using a hydrophilic initiator, we applied different hydrophobic initiators in order to prevent secondary nucleation in the continuous phase. Due to the nanoreactor situation, even at high conversions, still a low crosslinking degree and, therefore, low gel contents are obtained. The reduction of gel content is attributed to the high monomer-to-polymer ratio in the miniemulsion droplets, which possibly reduces the branching and, therefore, should delay the crosslinking [4]. It will be shown that the microstructure of the polymers obtained in miniemulsion at high temperature is similar to the microstructure obtained in a classical emulsion polymerization process at 5 °C. An up-scaling of the procedure is easily possible.

Experimental part

Materials

Sodium hydrogen carbonate (Merck, 99%), sodium dodecyl sulfate (SDS, Alfa Aesar, 99%), potassium oleate (EOC); 2,2′-azobis(2-methylbutyronitrile) (V59), 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70), 2,2′-azobis(2,4-dimethyl valeronitrile) (V65) (all initiators Wako Chemicals), hexadecane (Sigma-Aldrich, 99%), butadiene (Sigma-Aldrich, 99.8%), n-dodecyl mercaptane, and tert-dodecyl mercaptane (n-DM and t-DM) (both Sigma-Aldrich, 99%) were used as received. Styrene (Sigma-Aldrich, 99%) was distilled under reduced pressure before usage and was stored at 5 °C until use. Deionized water was used in all experiments. The cold polymerized technical SBR sample (EOC Group Belgium) was used as reference in some investigations.

Miniemulsion polymerization technique

Butadiene miniemulsion polymerization

Butadiene was condensed into a 10-mL pressurizable reaction vessel equipped with a polytetrafluoroethylene gasket, which was cooled with liquid nitrogen. The hydrophobe hexadecane (5 wt.% i.r. to monomer) and the initiator V65 (2 wt.% i.r. to monomer) were added to the frozen butadiene. To obtain a butadiene miniemulsion, the continuous phase consisting of an aqueous solution of potassium oleate or SDS (2 wt.%) buffered with sodium hydrogen carbonate (0.5 wt.%) was added onto the still frozen butadiene and allowed to thaw. After thawing, sonication with a Branson Digital Sonifier W450 equipped with a standard cup with a parabolic reflector at 90% amplitude twice for 10 min under cooling (0 °C) was performed, resulting in a homogeneous milky white miniemulsion. The net weight for all butadiene samples was 5 g. The miniemulsion was then polymerized at 50 °C in a Mini Hybridization Oven (Appligene Oncor, Germany) at 4 rpm overnight.

Styrene miniemulsion polymerization

The continuous phase, an aqueous SDS solution (0.3 wt.%) or an aqueous solution of potassium oleate (2 wt.%), was added to the dispersed phase, which was prepared by dissolving the oil-soluble initiator V59 (2 wt.% i.r. to monomer) and the hydrophobe hexadecane (4 wt.% i.r. to monomer) in distilled styrene. To obtain a styrene miniemulsion after 1 h of pre-emulsification by stirring at 2,000 rpm, the sample was sonicated using a Branson Digital Sonifier W450 equipped with a 1/2-in. tip at 90% amplitude for 2 min. To prevent thermal initiation, the sample was cooled in an ice bath during the homogenization process. The procedure results in a homogeneous white-opaque miniemulsion. The miniemulsion was then polymerized at 50 °C overnight. The total initial weight was 15 g for all samples.

Styrene–butadiene miniemulsion copolymerization

In the first step, a styrene precursor miniemulsion was prepared. The continuous phase was prepared by dissolving SDS in water or potassium oleate, respectively, in an aqueous sodium hydrogen carbonate (0.5 wt.%) solution. The oil-soluble initiator (2 wt.% i.r. monomers), hexadecane (4 wt.% i.r. monomers), and the transfer agent (n-DM or t-DM) were dissolved in styrene. The latter was combined with the continuous phase and stirred for 1 h at 2,000 rpm. Samples were sonicated using a Branson Digital Sonifier W450 equipped with a 1/2-in. tip at 90% amplitude for 2 min, resulting in homogeneous white-opaque miniemulsions. To prevent uncontrolled thermal initiation, the samples were cooled in an ice bath during the homogenization process. The total initial weight was 15 g for all samples.

To obtain the weight ratio of monomers, the desired amount of butadiene was condensed into a well cooled pressurizable reaction vessel. The precursor styrene miniemulsion was then added to the frozen butadiene and the reaction vessel was sealed tightly. The monomer mixture was homogenized by vigorously stirring. Polymerization took place under agitation at the desired temperature depending on the type of initiator used. All samples were polymerized for 14 h.

Upscaling experiments

The precursor styrene miniemulsions, following the same recipe as in microscale experiments, were prepared in an APV Gaulin (LAB2000) using a loop arrangement. The coarse emulsion is pumped through a narrow annular gap. The coarse emulsion is sheared by high pressure while passing the gap. This results in a finely dispersed system. The styrene miniemulsion is then charged in a pilot plant reactor (net volume 5 L) equipped with stirring, pressure, and temperature control. In the next step, butadiene is added to the system. A total amount of 3 kg styrene–butadiene miniemulsion was employed. Polymerization was performed at 50 °C for 12 h.

Characterization

The particle size of the polymeric nanoparticles was measured by dynamic light scattering (DLS) using a Zeta Nanosizer Nano ZS (Malvern Instruments, UK). For the measurement, 10 μL of the sample was diluted to 1 mL with water and measured in a PS standard sizing cuvette. DLS measurements give the cumulant mean size of the measured particles and the polydispersity index (PDI).

The solid content of the dispersion was determined by freeze drying the latex samples. The conversion was measured gravimetrically. The lyophilizate was used to characterize the microstructure via nuclear magnetic resonance (NMR), to determine the molecular weight distribution by gel permeation chromatography (GPC), and to measure the glass transition temperature by differential scanning calorimetry (DSC).

The nongel content was determined by dissolving 50 mg of sample in 10 mL toluene, stirring gently (300 rpm) for 24 h; after the samples were filtered through a 1-μm-pore-size filter, the filtrate was evaporated and the residue was weighed; the nongel part was determined by dividing the residue weight by initial weight.

GPC analysis was performed using a Dionex P580 pump, with a Waters 486 UV detector (λ=254 nm) and a Waters 410 RI detector using 5 μm bead size 8×300 mm SDV linear M columns from Polymer Standards Service in chloroform ($CHCl_3$), with a flow rate of 1 mL min^{-1} at 30 °C thermostatted column oven. Five milligrams of freeze dried sample was dissolved in 1 mL chloroform and filtered through a 1-μm syringe filter. The molecular mass of the samples was calculated with respect to PS standards and can, therefore, only reflect a relative value.

DSC was accomplished using a Perkin Elmer DSC-7. The glass transition temperature T_g of the dried sample was measured. Samples were sealed in 40-μL aluminum pans with a hole and measured from −140 to 50 °C for pure PB samples and from −140 to 120 °C for SBR and PS samples at a rate of 10 °C min^{-1} under nitrogen atmosphere.

^1H NMR and ^{13}C NMR (AMX 500, Bruker Instruments, Billerica, MA, USA) measurements were performed to analyze the composition and microstructure of the homopolymer and the copolymer. The signal assignment was done in accordance with spectral data reported by Sato et al. [6, 7]. The polymer compositions were calculated from integration of the NMR spectra. Therefore, 25 mg of the dried latex sample was dissolved in 0.7 mL of deuterated chloroform (δ=7.26 ppm). The terminal vinyl protons of the PB show a chemical shift of around 5 ppm; the respective carbon atom is shifted to 43.7 ppm in ^{13}C NMR measurements (pulse program: I-GATED). The signal at 5.6 ppm can be assigned to the protons of the double bond of the 1,4 isomers. In ^{13}C NMR measurement, the signals of the respective 1,4 trans and 1,4 cis C atoms show chemical shifts of 32.7 and 27.6 ppm, respectively. The signal at 43.7 ppm corresponds to the vinylic CH in the backbone of the PB chain. The relative areas of these peaks were integrated to calculate the microstructure composition of the PB.

The morphology of the polymeric nanoparticles was investigated by transmission electron microscopy (TEM). The diluted latex samples (diluted by factor 1,000) were fixed with 2% aqueous osmium tetroxide solution, which leads to a selective staining of the persistent double bonds in the PB fraction of the copolymer [8, 9]. The samples were then dehydrated in a graded series of 1-propanol embedded in Epon (Fluka, Germany). Ultra thin sections (approx. 80 nm) were imaged in a Philips 400 TEM (Fei, Eindhoven, The Netherlands) at an accelerating voltage of 80 kV.

Results and discussion

Cold SBR reference obtained by emulsion polymerization

Since PB and SBR latexes are produced usually via an emulsion polymerization process, a cold polymerized commercial SBR latex with high solid content (66.2%) was used as reference. A bimodal particle size distribution (107 and 559 nm) was detected by DLS and confirmed by TEM analysis (see Fig. 1). The TEM micrograph shows a strongly bimodal distribution of particle sizes. A quantification of the sizes is not possible due to the fact that the particles are embedded in EPON and cut. It shows that no microdomains of one of the polymers is formed, indicating a homogeneous statistically polymerized copolymer. Analysis by ^{1}H and ^{13}C NMR revealed a composition of 13 mol % PS and 87 mol% PB, consisting of 19% 1,2 PB units, 16% cis 1,4, and 52% trans 1,4 isomer units. A single glass transition point was found at −59 °C, confirming the homogeneous and statistical copolymer. However, the smaller particles of Fig. 1 are darker than the larger ones, indicating that they probably have a higher PB content. This conclusion is reasonable, as the solubility of butadiene in water is larger than that of styrene.

PB and polystyrene reference as obtained by miniemulsion polymerization

The low boiling point of butadiene (−4 °C) requires an adoption of the usual technique of the miniemulsion process for the formation of PB nanoparticles. Therefore, the butadiene was frozen in the reaction vessel and mixed with hexadecane as costabilizing hydrophobic component and the hydrophobic initiator V65. After the addition of the aqueous surfactant (potassium oleate) solution, the vessel was sealed and the temperature was allowed to rise. Sonication was performed in a sonifier equipped with a cup resonator, which enables the handling of pressurized samples. Polymerization was performed at high temperature (50 °C). The polymerization was started by using the hydrophobic initiator V65 in order to prevent secondary nucleation in the water phase.

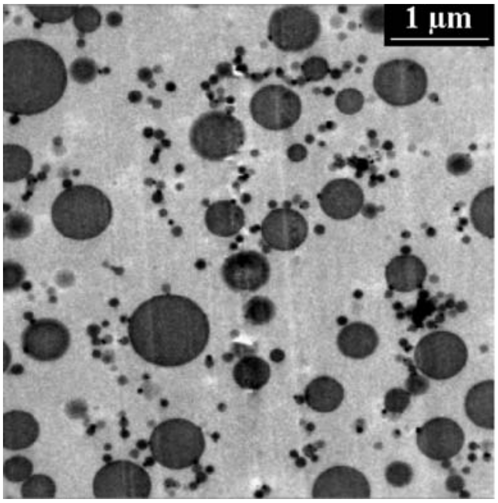

Fig. 1 TEM micrograph of SBR latex—ultrathin section (OsO_4 staining in EPON) showing a bimodal distribution of particles

The major characteristics of the reference PB miniemulsion latexes are shown in Table 1. All latex samples result in monomodal systems with a quite narrow size distribution.

The results of the DLS experiments were validated using TEM. The obtained micrographs show that homogeneous PB particles in the size range of about 100 nm (as one example, see Fig. 2) are obtained by the miniemulsion process. No large particles are detected.

The miniemulsion polymerization of butadiene results in high conversions of butadiene (usually about 90%); however, a slight tendency of decreasing conversion with increasing content of transfer agent (n-DM) is noted. The polymerization with 4.3 wt.% of n-dodecyl mercaptane gives the lowest conversion with 76%, other samples with lower amounts of transfer agent yield in much higher conversion of the monomer (Table 1). Please note that the values are averaged from several runs under the same conditions.

The freeze dried samples were used for further investigations concerning the molar mass, glass transition point, and microstructure of the resulting polymer depending on the transfer agent to monomer ratio.

The use of transfer agent changes—as expected—the molecular weight and its distribution, as well as the crosslinking and, therefore, the gel formation during polymerization significantly [10] (Table 1). Due to the nanoreactor situation, even at high conversions, still a quite low crosslinking degree and, therefore, low gel contents are obtained. The reduction of gel content was attributed to the high monomer-to-polymer ratio in the miniemulsion droplets, which possibly reduces the branching and, therefore, should delay the crosslinking [4].

The influence of n-DM on the number means of the molecular weight (M_n) is more pronounced than on M_w. The difference between the weight and the number average became even more explicit when compared to the industrially more relevant t-DM. Here, M_w shows only a slight reduction, and the transfer agent also provokes a lower downsizing of M_n.

Both transfer agents reduce the gel content significantly; however, full solubility of the homopolymer was only obtained for samples prepared with t-DM. To suppress gel formation completely, the addition of more than 3 wt.% t-DM with respect to the monomer is required.

The NMR measurements indicate compositions of the microstructure of 63% trans 1,4, 21.8% cis 1,4, and 15.2% vinyl isomer (for summary of the values obtained at 50 °C, see also Fig. 3). All samples prepared with n-DM and t-DM exhibit a homogeneous microstructure composition as shown by the small standard deviation given in Table 1. The influence of the transfer agent is found to be negligibly small.

Table 1 Characteristics of the PB latexes and their composition derived from NMR measurements and glass transition temperature T_g, 2 wt.% of surfactant was used with respect to continuous phase and 2 wt.% of the hydrophobic initiator V65 i.r. to the monomer was used; the reaction temperature was 50 °C

Sample No.	Transfer agent	Particle size z—average	PDI	Conversion	Nongel fraction	Molar mass		Polydispersity	Microstructure			T_g
	[wt.% i.r. to butadiene]	[nm]		[%]	[%]	M_w (RI) [g mol^{-1}]	M_n (RI) [g mol^{-1}]	PD	trans	cis	1,2	2. Heat [°C]
n-DM												
1	0.00	83	0.023	86	16	162,200	42,400	3.83	62.5	24.4	13.1	−82.0
2	0.00	123	0.021	~100	13	148,000	38,100	3.89	64.3	22.2	13.5	−81.7
18	0.52	104	0.031	91	18	152,900	34,500	4.43	62.9	20.1	17.0	−82.1
19	0.60	121	0.002	88	16	51,600	16,900	3.06	62.9	20.8	16.4	−81.9
23	0.88	102	0.026	88	17	48,000	15,400	3.13	64.1	21.8	14.1	−82.3
20	1.06	114	0.038	82	14	51,700	17,100	3.02	61.7	21.6	16.7	−82.3
22	2.51	121	0.022	90	27	51,000	8,800	5.80	64.9	21.4	13.6	−82.7
24	3.67	137	0.012	81	30	41,600	6,800	6.13	60.8	22.2	17.0	−84.0
25	4.30	132	0.025	76	27	43,300	10,500	4.14	63.3	21.5	15.2	−82.8
$\bar{x}$[a]									63.0	21.8	15.2	−82.4
σ[b]									1.3	1.2	1.6	0.7
t-DM												
10	3.65	147	0.048	66	77	138,600	31,300	4.43	62.1	21.1	16.8	−83.4
26	4.18	130	0.051	75	82	56,200	14,000	4.00	64.5	20.6	14.8	−83.1
15	4.92	143	0.013	72	92	120,200	18,000	6.68	62.1	20.5	17.4	−83.6
$\bar{x}$[a]									62.9	20.8	16.3	−83.4
σ[b]									1.4	0.3	1.3	0.3

[a] Average value

[b] Standard deviation

Further, the effect of the surfactant and polymerization temperature on the overall composition was investigated. SDS as standard model surfactant, the industrially widespread potassium oleate, and the hydrophobic azo-initiator V59 for polymerization at 72 °C were used for these experiments. Experimental data for the different initiator/surfactant systems are given in Table 2. The resulting polymers vary in their microstructure only slightly; the NMR data analysis reveals a slight decrease in the cis 1,4 in favor of the trans 1,4 fraction with decreasing temperature. No significant influence of the nature of the surfactant on the microstructure is found. The molar mass is reduced with increasing temperature, as expected.

We also investigated the polymerization at 30 °C, initiating the reaction by using V70. This set of experiments resulted in low conversion of monomer. The resulting latexes showed a multimodal particle size distribution, which was indicated by a high PDI value (>0.5). The molecular weights were not assessed due to the low conversion rates. However, the microstructure did not show a significant deviation.

The glass transition temperature of miniemulsion PB is significantly higher than for usually radically polymerized PB samples (Lit: −90 °C [11–13]; T_g (cis-PB)=−105 °C), indicating a higher trans ratio in the miniemulsion case. No pronounced effect of variation of the polymerization conditions is found on T_g (Table 1 and 2).

The reference pure polystyrene latex was also prepared via miniemulsion technique. The PS particles show a very

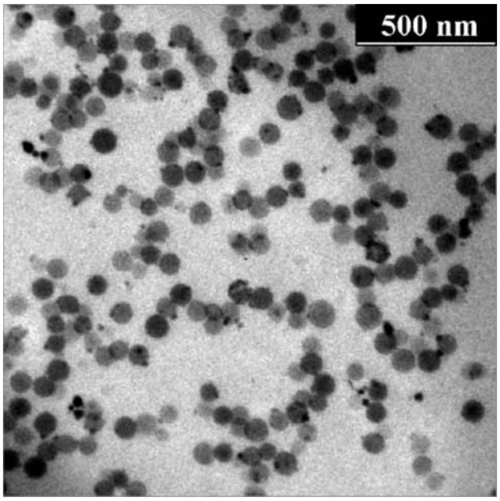

Fig. 2 TEM micrograph of a typical PB latex as ultrathin section (OsO_4 staining in EPON)

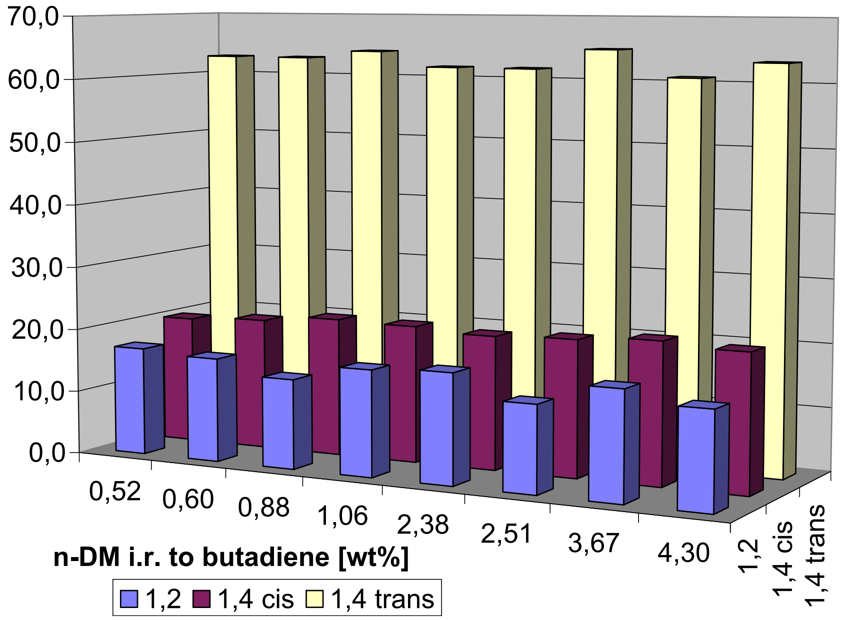

Fig. 3 Composition of PB samples prepared with n-DM at 50 °C

narrow size distribution. The z average of this sample is 109 nm and the PDI value for the oleate-stabilized system is 0.01; SDS, as surfactant, leads to monodisperse nanoparticles (PDI 0.02) with a size of 105 nm. A T_g of 74 °C (Lit: 105 °C [11–13]) can be attributed to the presence of hexadecane (see above). For further calculations concerning copolymer composition of the prepared styrene–butadiene latexes, this experimental T_g of the miniemulsion polystyrene was used. The molar mass of the resulting polymer was determined by GPC to be 3.82 10^5 g mol^{-1} for M_w and 6.41 10^4 g mol^{-1} for M_n.

Styrene–butadiene latexes

In the next step, copolymer particles with a weight ratio of butadiene to styrene of 75:25 were prepared. The procedure is an adaptation of the method used for styrene miniemulsion combined with the procedure to prepare the butadiene miniemulsion. At first, a styrene miniemulsion was prepared according to the standard recipe mentioned above. After freezing this miniemulsion, the calculated amount for the desired butadiene ratio was condensed on top. The sample was allowed to thaw slowly. Since the pressure

Table 2 PB latex samples prepared at 72 °C and at 50 °C to show the temperature dependency of the microstructure formed during polymerization

Sample No.	Transfer agent	Particle size z—average	PDI	Conversion	Surfactant	Molar mass		Polydispersity	Microstructure			T_g
	[wt.% i.r. butadiene]	[nm]		[%]		M_w (RI) [g mol^{-1}]	M_n (RI) [g mol^{-1}]	PD	trans	cis	1,2	2. Heat °C
T=72 °C, t-DM												
33	4.68	74	0.198	92	SDS	30,900	11,600	2.68	62.9	23.9	14.1	−82.9
34	3.71	82	0.228	88	SDS	33,400	10,400	3.21	61.0	23.2	17.2	−83.4
40	4.83	95	0.051	91	SDS	28,600	94,000	3.04	62.3	22.7	16.2	−83.2
$\bar{x}$[a]	4.41	84	0.159	90.3		31,000	10,500	2.97	62.06	23.27	15.84	−83.1
σ[b]	0.61	11	0.094	2.1		2,400	1,000	0.27	0.98	0.59	1.56	0.3
T=72 °C, t-DM												
39	4.82	105	0.163	~100	K-Oleate	26,200	9,400	2.78	61.9	23.2	16.1	−84.5
41	4.06	104	0.114	99	K-Oleate	27,500	7,000	3.92	63.1	23.0	14.9	−83.3
$\bar{x}$[a]	4.44	105	0.138	99.5		26,800	8,200	3.35	62.51	23.12	15.48	−83.9
σ[b]	0.54	0.7	0.035	0.7		923	1,700	0.80	0.83	0.14	0.80	0.8
T=50 °C, t-DM												
43	3.64			100	SDS	46,500	11,900	3.92	62.7	21.0	17.7	−82.8

[a] Average value

[b] Standard deviation

building up during the thawing step is sufficiently high, the butadiene stayed liquid. Then, the butadiene was allowed to diffuse into the styrene monomer droplets for 30 min. After this step, the reaction was performed at elevated temperature. Due to the hydrophobic initiator, the homopolymerization of butadiene could be prevented.

Similarly as above, the samples were stabilized with SDS (samples A-72, C- and D-30, F- to J-50) as a model system [3] or with the industrially more relevant potassium oleate (samples K- to W-50 including samples 2- and 3–50). The miniemulsion procedure had to be adapted to the change of surfactant. Hence, the pH of the continuous phase was adjusted to pH 9 by $NaHCO_3$ in order to ensure the presence of deprotonated COO head groups of the surfactant.

For the oleate-stabilized samples, we showed that the miniemulsion approach is also suitable for high-solid-content latexes up to 60%. The samples still show a narrow and usually monomodal size distribution and appear stable and coagulum-free for several months.

In the following, the samples were investigated by DSC, showing a single T_g for all prepared copolymer samples, which indicates the formation of a statistically formed copolymer. From the T_g, the copolymer composition was calculated according to the Gordon–Taylor equation [14, 15], confirming the results by NMR analysis.

Influence of the reaction temperature

Reaction temperature of 72 °C

Using V59 as initiator, the reaction could be performed at 72 °C. The particle size of the samples is around 130 nm with a small PDI value, which indicates a narrow distribution in both latex samples. From DSC analysis, a composition of 15 wt.% PS and 85 wt.% PB was determined. Due to low solubility, ^{13}C NMR experiments could not be consulted for the evaluation of the composition. Therefore, we only determined the polystyrene/PB ratio and 1,2 fraction of PB by ^1H NMR spectroscopy. The PB fraction was calculated to be 92 mol%, of which one fifth is comprised of 1,2 units. Similar results are reported for emulsion-polymerized SBR (E-SBR) in literature [16]. The slight difference in the value obtained by DSC lies

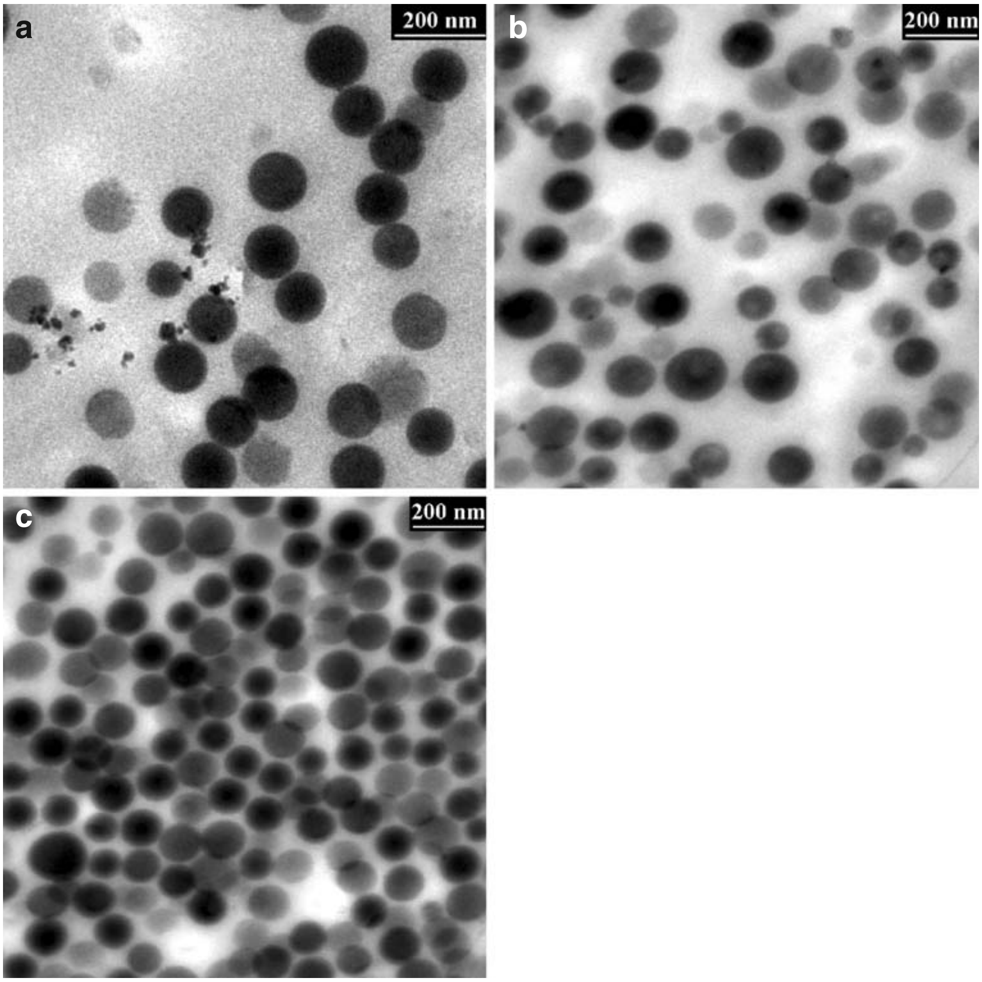

Fig. 4 TEM micrographs of a typical SBR latex as ultrathin section (OsO_4 staining in EPON) **a** polymerized at 72 °C **b** polymerized at 30 °C; **c** polymerized at 50 °C

within the error of the Gordon–Taylor method. The formation of a homogeneous statistical copolymer is affirmed by the appearance of a single glass transition point in DSC. Also in TEM, each particle appears uniformly stained by the OsO_4 treatment, which indicates that the copolymer is consistent even in the core of the particles (Fig. 4). The different shadowing between the nanoparticles may indicate a slight variation of the butadiene composition from one particle to the other.

Reaction temperature of 30 °C

Polymerizations at 30 °C result in stable, quite narrowly distributed latex samples. However, the conversion data show low values of just above 50%, indicating that V70 is unsuitable to lead to high conversion in convenient polymerization time, which might possibly be due to the relative importance of the termination rate, which is higher

Table 3 Major characteristics of latex samples: particle size, PDI, solid content, conversion rate, microstructure, and glass transition temperature

Sample No.	Butadiene	Surfactant		Transfer agent[a]	theoretical SC	Experim. SC	Particle size z average	PDI	T_g	Copolymer composition Gordon–Taylor eq.	Copolymer composition by NMR			
	[wt.%]	[wt.% i.r. to continuous phase]	[wt.% i.r. to monomer]	[wt.% i.r. monomer (s)]	[wt.%]	[wt.%]	[nm]		[°C]	[wt.% of PB in PB-co-PS]	[mol % PB in PB-co-PS]	1,2	1,4 trans	1,4 cis
Reference											87.0	19.1	59.6	21.3
SDS as surfactant														
V70 as initiator; T=30 °C														
$\bar{x}$	73.25	1.40	3.29	1.59	31	17	81	0.13	−60.6	76.5	83.6	15.2	63.5	21.4
σ	2.76	0.00	0.44	2.25	3	0	13	0.08	3.5	3.8	1.5	1.3	2.3	1.1
V59 as initiator; T=72 °C														
A-72	76.70	1.40	2.72	4.45	35	33	134	0.01	−71.1	85.4	92.6	20.6	–	–
V65 as initiator; T=50 °C														
$\bar{x}$	76.94	1.40	2.77	3.14	35	30	107	0.05	−67.8	82.5	91.1	17.6	54.6	27.8
σ	0.61		0.07	0.69	0.5	2	5	0.04	1.2	1.2	0.5	1.2	3.8	4.1
K-Oleate as surfactant														
V65 as initiator; T=50 °C														
$\bar{x}$	76.55	2.00	3.71	3.82	36	28	107	0.04	−61.9	77.1	92.8	20.6	53.4	26.1
σ	0.92			0.13	0.5	2	18	0.01	1.5	1.3	1.0	3.0	2.7	5.6
Increase of solid content—V65 as initiator; T=50 °C														
$\bar{x}$	76.73	3.00	3.07	3.75	51	41	102	0.13	−62.7	77.7	91.7	20.1	56.3	23.6
σ	0.74	1.00	0.73	0.14	2	4	24	0.09	0.9	0.8	2.2	1.0	1.7	2.3
High solid content latex														
$\bar{x}$	75.00	9.00	4.24	3.85	70	61	112	0.11	−67.0	81.6	93.1	18.5	56.0	25.1
Σ					0.2	0.4	28	0.10	0.6	0.6	0.6	2.6	0.4	3.0
Upscaling sample														
2–50	75.00	2.00	4.45	4.00	31	24	119	0.05	−57.6	74.4	88.2	19.9	55.2	24.9
3–50	75.00	2.00	4.67	4.00	30	27	108	0.02	−59.3	74.8	86.5	18.1	58.4	23.5
$\bar{x}$	75.00	2.00	4.56	4.00	31	25	114	0.03	−58.5	74.6	87.4	19.0	56.8	24.2
Σ	0.00	0.00	0.16	0.00	0.7	2	8	0.02	1.2	0.3	1.2	1.3	2.2	1.0
Variation of transfer agent content—V65 as initiator; T=50 °C														
R-50	76.10	4.00	4.70	0.55	49	40	109	0.23	−59.1	74.6	87.5	17.3	52.5	30.1
S-50	76.40	4.00	4.51	1.07	49	40	119	0.05	−60.1	75.5	90.4	18.6	58.0	23.4
T-50	76.20	4.00	4.51	2.02	49	39	108	0.02	−63.3	78.3	88.4	18.5	57.7	23.9
W-50	76.60	4.00	4.51	2.97	50	36	168	0.21	−68.3	82.8	91.1	19.8	56.5	23.8
V-50	76.10	4.00	4.51	3.88	50	38	110	0.04	−64.6	79.4	89.5	17.9	57.6	24.5
U-50	76.60	4.00	4.33	5.47	50	37	160	0.28	−62.2	79.3	88.8	17.9	57.6	24.5
$\bar{x}$												18.3	56.6	25.0
Σ												0.8	2.0	2.5

[a] Samples A–Q. Samples 2–50 were prepared with n-DM; samples 3 and R-50 to W-50 were prepared with t-DM

at lower temperatures, as the energy of activation of the termination reaction is lower than that of propagation.

Still, the resulting latex shows a single T_g, which indicates the formation of a statistical copolymer. Also, TEM analysis confirms this result (see Fig. 4b). The polymerization at low temperature results in a slightly higher glass transition temperature compared to the samples prepared with V65 and V59. From integration of the ^{1}H NMR spectrum, the PB-to-polystyrene ratio was calculated to be slightly lower in the copolymer, which explains the higher glass transition temperature. In addition to this, the ^{13}C NMR spectrum for this latex shows a small deviation from other samples. The PB fraction in the copolymer is comprised of 21% cis 1,4, 64% trans 1,4, and 15% 1,2 units. With respect to the 1,2 units, the low temperature leads to a slightly lower fraction compared to samples polymerized at higher temperatures (see above). Therefore, the proportion of 1,4 is slightly higher; a significant change appears for the trans configuration, which is favored at lower temperatures as the thermodynamically more stable isomer (see Table 3). The here-reported values are similar to E-SBR compositions reported in literature [17].

Reaction temperature of 50 °C

For samples polymerized at 50 °C, the initiator V65 was used. This temperature was chosen as an intermediate state with further parameters to be varied (surfactant, solid content, upscaling, transfer agent, see below). Here, we prepared a first set of latexes with n-DM as transfer agent and SDS as surfactant. The major characteristics of these samples are given in Table 3. The increase in polymerization temperature and the variation to the respective initiator lead to high conversions of more than 80%. Particles are narrowly distributed and show an average particle size of approximately 100 nm (see Fig. 4c).

In a second row of experiments with potassium oleate as surfactant, n-DM was applied as transfer agent. Neither the change of the stabilizer nor the minor change in the amount of surfactant used to generate stable and monodisperse miniemulsion latexes led to significant deviation. The so far described samples all have a solid content of below 40 wt.%. In the following experiment scheme, we adapted our established system to higher theoretical solids. Hence, we changed the surfactant-to-water ratio quite significantly; however, this step-up does not lead to a major difference in the overall system. With respect to the dispersed phase of these samples, the ratio was only raised by approximately one fourth, so the system is still well below the cmc since the available interface is very large due to the small droplet size resulting from the miniemulsion process.

In the first step, we raised the theoretical solid content to 51 wt.%, which resulted in latexes with a solid content of around 41 wt.%. Again, high conversions of an averaged 80% were obtained after overnight polymerization. For industrial applications of SBR latex, the solid content is above 50 wt.%; therefore, we synthesized samples with a solid content of averaged 61 wt.% at a conversion rate of 86%. The high solids do not influence the monomodality of the particle size distribution; however, we still obtained particles of an average size of 110 nm with a PDI of 0.1. The microstructure, as well as the molecular weight distribution, proves to be independent of the ratio of dispersed to continuous phase.

The last set of experiments dealt with the influence of the transfer agent t-DM. Here, the transfer agent-to-monomer ratio was varied between 0.5 and 5.5 wt.%. The first two values of M_w for 0.5 and 1 wt.% of t-DM are very low; here, we assume that only a minor part of the copolymer was dissolved because the gel fractions of these samples are still around 20%. Apparently, for the samples prepared with more than 2 wt.% t-DM, higher values for M_w are obtained; a reduction of the molecular weight with increasing transfer agent ratio could still be observed. For the number mean M_n, a slight decrease is detected with the rise of t-DM ratio. The gel content was reduced with increasing amount of transfer agent significantly to almost full solubility of the resulting copolymers. The increase of the soluble fraction depending on the transfer agent ratio is shown in Fig. 5.

Influence of the type and amount of surfactant

As mentioned above, the influence of the surfactants on the microstructure, conversion, etc., is negligible; the system has to be adjusted by only minor changes since the two surfactants SDS and potassium oleate show different characteristics. The stabilization effect of potassium oleate

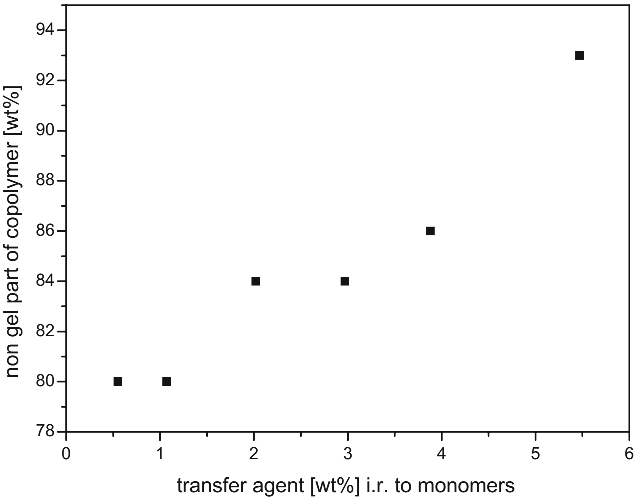

Fig. 5 Nongel part of copolymer dependent on t-DM ratio

is pH sensitive; therefore, the addition of sodium hydrogen carbonate is essential to keep the pH constant during and after polymerization.

The average size of the particles using SDS is smaller compared to the oleate-stabilized dispersion; however, the narrow size distribution of the resulting latexes is given for both systems, as indicated by the low PDI values as shown in Table 3.

Up scaling experiments

In order to prove the applicability of the presented method as an industrially relevant process, up scaling experiments to a total amount of 3 kg dispersion with a solid content of around 30 wt.% were performed. In the first experiment, the transfer agent n-DM (4 wt.% i.r. to monomers) was used; in the second experiment, it was replaced by the same amount of t-DM.

Both resulting SBR latexes show a narrow particle size distribution in the region of 110 nm with a PDI below 0.05. The gel content in the case of the sample prepared with n-DM is 28%, which again leads to a low M_w of 120,000 g/mol, the change to t-DM leads to a reduction of the gel content to 6%, and a rise of the M_w to 440,000 g/mol. The microstructure of the samples is quite similar to the ones obtained from microscale experiments. However, the incorporated amount of butadiene is reduced to 87%; a comparably low incorporation rate was only found in the samples polymerized at 30 °C.

Conclusion

In this article, we presented the miniemulsion polymerization—a new heterophase polymerization route—of the gaseous monomer butadiene, as well as the copoymerization of the same with styrene. The miniemulsion approach, which was so far solely employed in systems that are in the liquid state at standard conditions, was modified for the purpose of polymerizing liquified (under pressure) systems. Once the butadiene is pressurized, the miniemulsion approach can readily be applied using a cup resonator for the miniemulsification by ultrasound. All here-presented PB latexes are stable, showing a monodisperse particle size distribution and a long-term stability over several weeks. The microstructure analyses of the dried latex samples clearly illustrate the stable composition of the PB conformers. As described for emulsion polymerization in literature, the influence of transfer agents like the mercaptanes used on the microstructure is not significant.

The miniemulsion copolymerization of butadiene and styrene in the industrially most interesting weight ratio of 75:25 was demonstrated. These SBR latexes all are of a milky white appearance; the latexes are all monomodal with respect to particle size distribution for both surfactant systems used in these investigations. The SBR samples are stable over several months; no coagulum formation was observed. We also investigated the influence of different polymerization temperatures, which did not lead to significant microstructural changes in the resulting copolymer. Only slight changes, especially in the trans 1,4 components of the PB fraction, were detected. The molecular weight distribution and the amount of gel fraction can be reduced significantly by the use of the transfer agents, as found for emulsion polymerization; here, the t-DM is more efficient in the reduction of gel.

The presented methodology of miniemulsion polymerization for the preparation of the industrially highly relevant SBR system shows that, contrary to common techniques ("cold" and "hot" rubber), the structural characteristics of the copolymer are fairly tolerant to variations of the synthesis parameters, especially to temperature. On the other hand, the molecular weight can be easily adjusted by the application of transfer agents while the insoluble gel content is substantially reduced.

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