

Preparation and SEM Characterization of Sterically Stabilized Polystyrene Particles

^aI. CAPEK*, ^bL. CHITU, ^aS. JANÍČKOVÁ, ^cI. KOSTIČ, ^bŠ. LUBY, ^bE. MAJKOVÁ, and ^dA. ŠATKA

^a*Polymer Institute, Slovak Academy of Sciences, SK-842 36 Bratislava*

^b*Institute of Physics, Slovak Academy of Sciences, SK-845 11 Bratislava*

^c*Institute of Informatics, Slovak Academy of Sciences, SK-842 31 Bratislava*

^d*International Laser Center, SK-812 19 Bratislava*
e-mail: upolign@savba.sk

Received 17 September 2003

Batch emulsion polymerization of styrene was used to prepare the polystyrene particles. The emulsion polymerization was initiated either by the water-soluble initiator ammonium peroxydisulfate (APS) or the oil-soluble initiator 2,2'-azobisisobutyronitrile (AIBN). The nonionic emulsifier Tween 20 was used to stabilize the polymer particles. The polymerization rate *vs.* conversion dependence was characterized by three rate intervals. The APS-initiated polymerization was faster than the AIBN-initiated one. The polymer particles prepared by the APS-initiated emulsion polymerization were less monodisperse than those prepared by the AIBN-initiated polymerization. The (ordered monolayer) hexagonal arrangement of polymer particles prepared by the AIBN-initiated polymerization appears at the high emulsifier concentration or the large mass ratio emulsifier/monomer. The ordered SEM particle structures are initiated by the interpenetration of the thick interfacial layers of neighbouring polymer particles. The presence of charged groups in the emulsifier layer or the loosely organized emulsifier layer disfavours the ordered particle structures.

Nonionic emulsifiers of the alkyl- or arylpolyethylene oxide (PEO) type are very popular as emulsion stabilizers. They enhance the chemical and freeze-thaw stability of the latex products. The coarse polymer emulsions are formed by emulsion polymerization stabilized by nonionic emulsifier [1, 2]. The colloidal stability of polymer latex stabilized by the PEO-type nonionic emulsifier is nearly independent of electrolyte concentration but it is temperature-dependent. The extension of PEO chains into the aqueous phase decreases with increasing temperature. The excellent ability of nonionic emulsifiers to solubilize and disperse hydrophobic oils such as fats and mineral oil in water leads to extensive use of this type of emulsifier. Nonionic emulsifier adsorbs only marginally to make hydrophilic surfaces hydrophobic or hydrophobic surfaces hydrophilic and differs from the results obtained with most ionic emulsifiers [3]. In the sterically stabilized dispersions the colloidal stability of polymer particles is provided by steric repulsion between approaching particles [4, 5]. The thick surface layer formed by nonionic emulsifier makes a barrier for particles approaching one another.

The surface capping of particles by organic surfac-

tant prevents their agglomeration and controls their regular distribution on the substrate. We speak about self-assembling of particles. Physical properties of particles depend on their dimensions, therefore their size distribution should be narrow (the best results refer to $\approx 5\%$). Particles are of spherical, cylindrical, pyramidal or other shapes. Self-assembled arrays of particles (2- or 3-dimensional lattice) are relatively small up-to-now; usually they cover the area of only a few $100\ \mu\text{m}^2$ or less. Their lateral periodicity can be triangular, square, hexagonal, *etc.* [6]. The array formation mechanism is not well understood up-to-now, it is first of all affected by the type of surfactant and type of the substrate.

Various experimental methods are available for measurement of the size and size distribution of polymer particles [7]. For example, the dynamic light scattering estimates the diffusion coefficient. For relatively hard particles the particle size can be determined with sufficient precision by scanning electron microscopy (SEM) or transmission electron microscopy (TEM). However, the electron beam can distort soft particles, cause shrinkage of particles and problems appear when agglomeration has occurred.

*The author to whom the correspondence should be addressed.

In the previous works [8, 9] we have studied the sterically stabilized microemulsion polymerization of styrene at different temperatures. It was found that the rates of particle formation and polymerization strongly increased with increasing temperature. The main item of this work is the preparation of the polymer particles by the batch emulsion polymerization of styrene stabilized by a nonionic emulsifier. Variations of kinetic and colloidal parameters with the initiator type – the water-soluble initiator ammonium peroxodisulfate and oil-soluble initiator 2,2'-azobisisobutyronitrile – are investigated. The self-assembling of sterically stabilized polystyrene particles into monolayers and the size and distribution of polymer particles are investigated by SEM.

EXPERIMENTAL

Commercially available styrene (St, Fluka) was purified by distillation under reduced pressure. Extra pure ammonium peroxodisulfate (APS, Fluka), 2,2'-azobisisobutyronitrile (AIBN, Fluka), and NaHCO_3 were used as supplied. The nonionic emulsifier used was the reagent-grade Tween 20 (Tw 20, polyoxyethylene sorbitan monolaurate, provided by Serva in the form of a 97 % aqueous solution). The reagent-grade sodium dodecyl sulfate (SDS, Fluka) and cetyltrimethylammonium bromide (CTAB, Fluka) were used. Doubly distilled water was used as a polymerization medium.

Batch emulsion polymerizations of styrene were carried out at 60 °C with the recipe comprising 100 g water, 5 g Tw 20, 10 g styrene, 0.016 g NaHCO_3 , and 0.0164 g AIBN or 0.0152 g APS. The homogenizer (Ultra Turrax, IKA Works, USA) was used to prepare the homogenized monomer emulsion (miniemulsion) for the polymerization. The monomer conversion was determined by the dilatometric method and the final conversion of systems with higher monomer concentration was checked by gravimetry. The polymerization technique and the preparation of polymer latex for particle size measurements were described earlier [10, 11]. The measurements of average size of polymer particles were performed by a static light scattering method as determined earlier [12, 13].

Particle size and particle size distribution were calculated using SEM data from the number and mass average diameters (D_n and D_m) as follows

$$D_n = \frac{\sum(N_i D_i)}{\sum(N_i)},$$

$$D_m = \frac{\sum(N_i D_i^4)}{\sum(N_i D_i^3)}$$

$$D_m/D_n = \text{polydispersity index (PDI)}$$

where N_i is the number of particles with diameter D_i .

The volume-average particle size (D_v) was calcu-

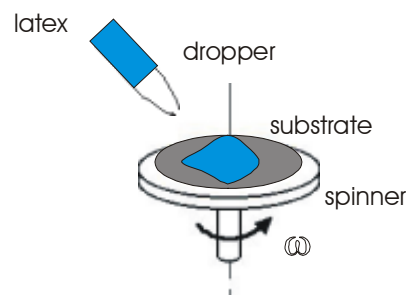


Fig. 1. Scheme of the spin coating method.

lated with the following equation

$$D_v = \left\{ \frac{\sum(n_i D_i^3)}{\sum(n_i)} \right\}^{1/3}$$

Spin Coating

The layers of particles can be deposited onto substrates by drying of drops, by spin coating or by Langmuir–Blodgett technique [14]. Spin coating has been used for several decades and it is the preferred method for application of thin, uniform films to flat substrates. This process is very simple, illustrated in Fig. 1. The original emulsion containing *ca.* 10 mass % polystyrene particles was diluted by water in the ratio: 10 cm³ of water/1 mm³ of polystyrene (PSt) original emulsion. 20 mm³ of diluted dispersion was injected on the surface of glass substrate. The substrate is then rotated at suitable speed in order to spread the fluid by centrifugal force. Rotation is continued for some time, with fluid being spun off the edges of the substrate, until the desired film thickness is achieved. Final film thickness and other properties will depend on the nature of the liquid (viscosity, drying rate) and the parameters chosen for the spin process. The rotation speed of the spin coater was fixed to be 800 min⁻¹. In order to regulate the deposition of polystyrene particles (balls) we have modified the surface of glass substrate with the negatively charged surfactant. Deposition of charged latex particles on oppositely charged glass substrate is driven by electrostatic attraction and a layer of latex particles covering the surface is achieved. Microscopic slides were treated with SDS to provide the glass with a negative charge. The pieces of glass are immersed in SDS solution for 45 min. Then the glass slide was vertically suspended in a latex dispersion at room temperature for 10 min. Finally the coated substrate was dried in air. The experiments were achieved at room temperature.

RESULTS AND DISCUSSION

The conversion—time data for the sterically stabilized emulsion polymerization of styrene initiated

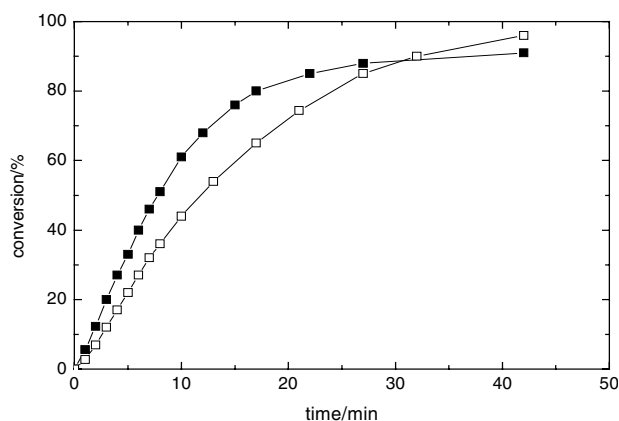


Fig. 2. Variation of monomer conversion in the emulsion polymerization of styrene with the initiator type and reaction time. ■ APS, □ AIBN.

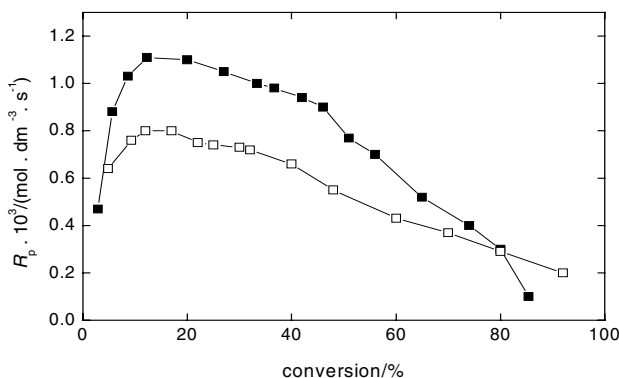


Fig. 3. Variations of the rate of emulsion polymerization of styrene with the initiator type and conversion. ■ APS, □ AIBN.

by a water-soluble initiator (APS) and oil-soluble initiator (AIBN) are shown in Fig. 2. The conversion curves become concave downward at medium conversion. The polymerization becomes much slower at *ca.* 80–90 % conversion and the decrease is much more pronounced in the APS-initiated polymerization. The slower polymerization is due to the increased aqueous phase termination and the formation of more hydrophilic oligomeric radicals. The entry efficiency of more hydrophilic oligomeric radicals into the hydrophobic polystyrene particles is decreased.

Variations of the polymerization rate in the emulsion of styrene with the initiator type and conversion are illustrated in Fig. 3. For both initiators the polymerization consists of three rate intervals. First the rate of polymerization abruptly increases to the maximum reaching *ca.* 15–20 % conversion (Interval 1). The abrupt increase in the initial polymerization rate ($R_{p,init}$) can be attributed to the robust particle nucleation. The second rate interval starts from 10 % conversion and ends at 50 % conversion. The onset of the third rate interval is at *ca.* 50 % conversion and the

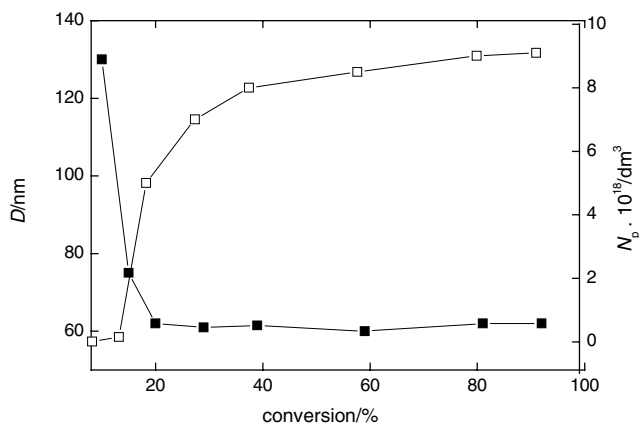


Fig. 4. Variation of the particle diameter (D , ■) and the number of polymer particles (N_p , □) with conversion.

rate strongly decreases to the final conversion. In all the three intervals the polymerization is always faster in the APS-initiated case. The higher rate of radical formation in the aqueous phase and consequently the larger entry rate of radicals from the aqueous phase to the polymer particles in the APS-initiated polymerization are responsible for the faster polymerization.

Fig. 4 shows that the large particles (*ca.* 200 nm) appear shortly after the start of polymerization. The appearance of large particles is attributed to the accumulation of small amounts of polystyrene oligomers in the monomer droplets [15, 16] and/or the presence of nonionic emulsifier in the monomer phase (droplets) [17]. In both cases the stability of monomer droplets (the highly monomer-swollen polymer particles) increases. The restricted diffusion of monomer from the stable monomer droplets to the reaction loci can be responsible for the slight decrease in the polymerization rate with increasing conversion in the second interval (Fig. 3).

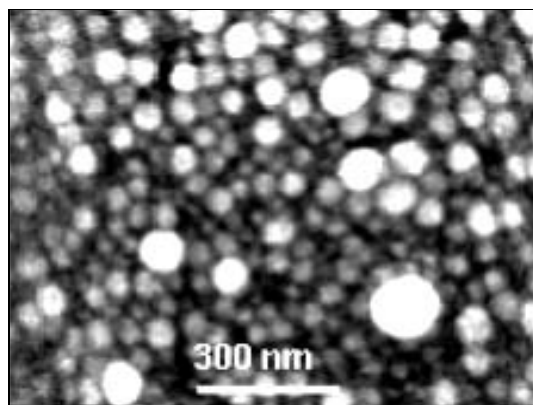
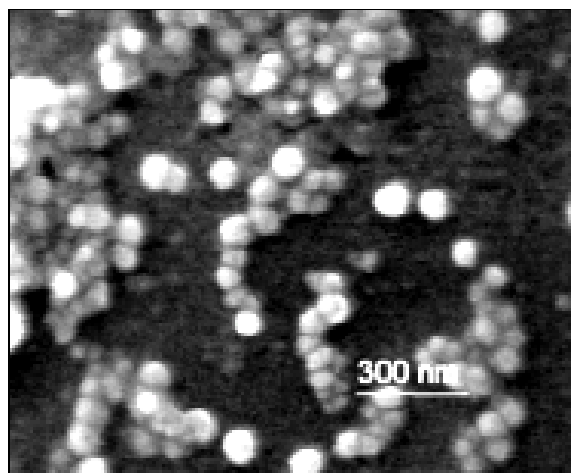
The number of polymer particles (N_p) increases up to high conversion and the increase is much more pronounced at low conversion (Fig. 4). The abrupt initial increase in the rate of polymerization can be attributed to the abrupt increase in N_p . In the low conversion interval (up to 20 % conversion), the rate of particle formation is very high. The presence of large number of microdroplets or minidroplets favours the particle nucleation. The high oil solubility of emulsifier indicates that the large fraction of initial emulsifier is dissolved in the monomer droplets. The continual consumption of monomer (monomer droplets) is accompanied with the release of emulsifier from the monomer droplets to the aqueous phase which is available for the further particle nucleation and stabilization. The continuous release of emulsifier from the monomer phase can contribute to the particle nucleation at very high conversion.

The particle size and particle size distribution of polystyrene particles estimated by SEM are summa-

Table 1. Colloidal Parameters of Polymer Particles Prepared by the APS-Initiated Emulsion Polymerization Characterized by SEM

Sample	$\frac{D_n}{\text{nm}}$	$\frac{D_m}{\text{nm}}$	PDI	$\frac{D_v}{\text{nm}}$	c_{disp}^a	Conditions
1	52	76.6	1.47	89.67	10	Spin coating (800 min^{-1}), room temperature
2	59.3	72.4	1.22	78.92	10	Dried in air, room temperature
3	58.64	60.47	1.031	55.78	10	Dialysis, spin coating
4	48.91	84.03	1.72	56.71	10	Dialysis, dispersion treated with CTAB, then drop injected on the substrate deposited with SDS

a) c_{disp} (volume of original dispersion in 100 cm^3 water)/ mm^3 .

**Fig. 5.** SEM micrograph of a drop of 20 mm^3 latex solution dried on glass substrate by spin coating.**Fig. 6.** SEM micrograph of a drop of 20 mm^3 latex solution (after dialysis) dried on glass substrate by spin coating.

rized in Figs. 5–10 and Tables 1 and 2. Figs. 5–7 show the particle size data for the polystyrene particles prepared by the APS-initiated emulsion polymerization and Figs. 8–10 summarize the particle size data for the polystyrene particles prepared by the AIBN-initiated emulsion polymerization. The hydrodynamic particle diameter (D_{LS}) estimated by the light scattering method was 62–64 nm for the APS-initiated polymerization and after six-month storing at room temperature it increased up to 68 nm. The hydrodynamic particle diameter of polystyrene particles prepared by the AIBN-initiated polymerization was 50–54 nm and it increased after the six-months storing at room temperature to *ca.* 72 nm. These results indicate that the polymer particles prepared by APS are more stable than those prepared by AIBN. In the former case the electrical double layer around the particles can be responsible for the increased stability. The electrical double layer is formed from the entering surface-active oligomeric radicals derived from the APS radicals. The charge of the oligomeric radicals comes from the primary radicals generated by the decomposition of APS. The polymer particles formed in the AIBN-initiated polymerization have no charge and therefore the particle agglomeration is more pronounced.

The diluted polymer dispersion was used to prepare the monolayer of polystyrene particles on the

glass substrate by spin coating (Fig. 5, Table 1, sample 1). The SEM micrograph shows the dense monolayer of polymer particles but the polystyrene particles are not clearly distinguished. This can be attributed to the presence of larger amount of free emulsifier that during the drying process accumulates on the particle surface. Consequently, the volume-average particle size determined by SEM is larger than the hydrodynamic particle size ($D = 62 \text{ nm}$). The close-packing of PSt particles or strong interaction among particles caused by spin coating increases the polydispersity of polymer particles. The increased interaction and agglomeration of polymer particles initiate the formation of larger particles as it was confirmed by SEM. The formation of large particles can also result from the nucleation of large monomer droplets after the start of polymerization as it was confirmed by the light scattering (Fig. 4).

When the monolayer is prepared by simple drying of deposited polymer dispersion at room temperature the polydispersity index is decreased (Table 1, sample 2). The depressed interparticle interaction suppresses the agglomeration of polymer particles. In the next approach the polymer dispersion was deprived of free emulsifier by dialysis (Fig. 6, Table 1, sample 3).

Under such conditions the polydispersity of poly-

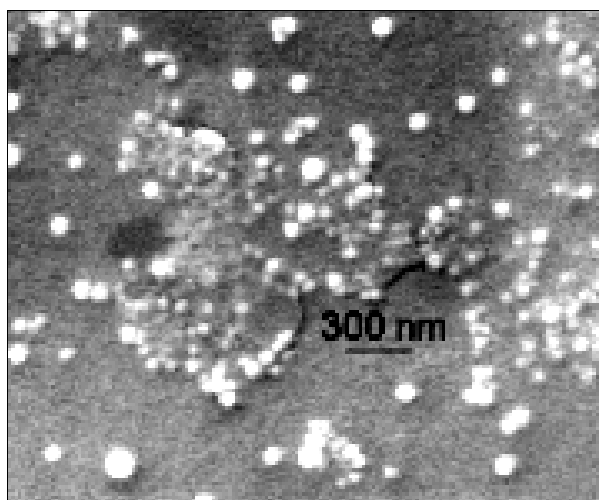


Fig. 7. SEM micrograph of a polymer latex on the glass substrate pretreated with SDS and then dropped in vertical position into latex solution.

mer particles is strongly reduced as well as the volume-average particle diameter (Table 1). The low level of free emulsifier decreases the thickness of emulsifier layer at the particle surface and the degree of overlapping of emulsifier layers of interacting particles. This is accompanied with the decrease in the particle agglomeration. The exchange of the polar groups of nonionic emulsifier Tween 20 with the cationic groups of ionic emulsifier CTAB strongly increases the polydispersity index (Fig. 7, Table 1, sample 4). This could result from the depressed surface charge of polymer particles caused by the adsorption of Tween 20 on the surface of CTAB-stabilized polymer particles.

The monolayer of polystyrene particles without surface charge was prepared from the diluted emulsion drying at room temperature (Fig. 8*a*, Table 2,

sample 2). The high level of emulsifier is accompanied with the formation of continual well-organized particle monolayer. The absence of partial surface charge in the interfacial layer favours the organized assembling of polymer particles during the drying process. Under these conditions the monolayer of polymer particles with higher degree of the monodispersity appears as it is revealed by SEM. The monodispersity of polymer particles was more pronounced in the sample with lower concentration of polymer particles (Table 2, sample 1). This indicates that the organized assembling of particles proceeds under the certain critical time or condition during which they first interact and then their layers penetrate one another. In the case that there are some obstacles against the particle shells penetration such as the presence of charged groups or the shrunk emulsifier layer, the mutual penetration of particle surface (emulsifier) layers does not proceed and the nonorganized aggregates appear. However, the polydisperse polymer dispersions and the nonorganized monolayers were detected when the PSt latex was aged for 3 months (Fig. 8*b*) and then used.

Spin coating strongly decreases the quality of SEM micrograph and the sharpness of polymer particles (Fig. 9, Table 2, sample 3). The spin coating increases the particle concentration at the SEM micrograph domain due to which the interparticle interactions increase and so the formation of particle agglomerates. This procedure is accompanied by the increase in the particle size and particle distribution in the particle monolayer. The monolayer of the sample with higher concentration of polymer particles pretreated with dialysis is shown in Fig. 10 (Table 2, sample 4). This micrograph indicates that dialysis does not improve the arrangement of polymer particles within the monolayer. On the contrary,

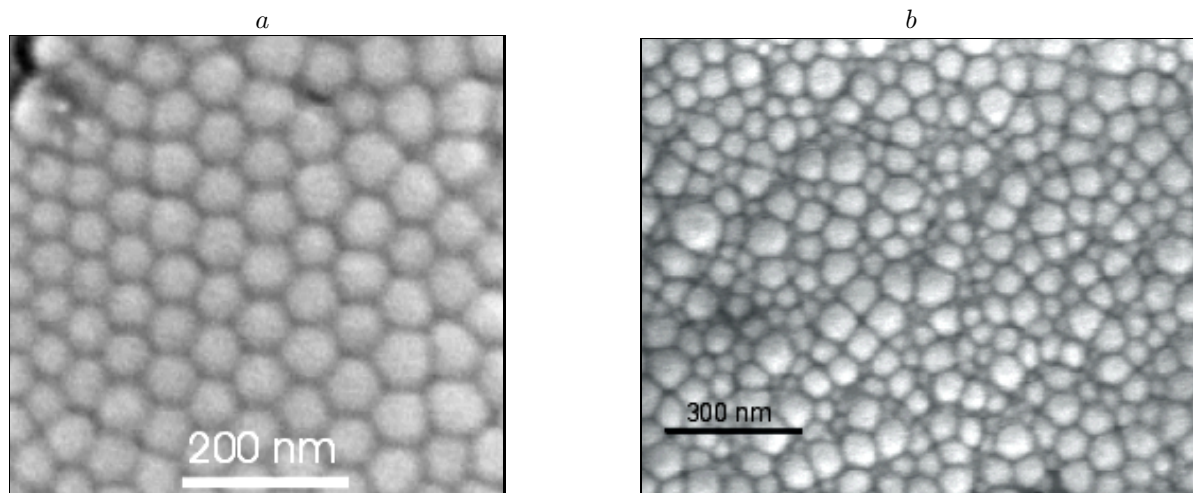
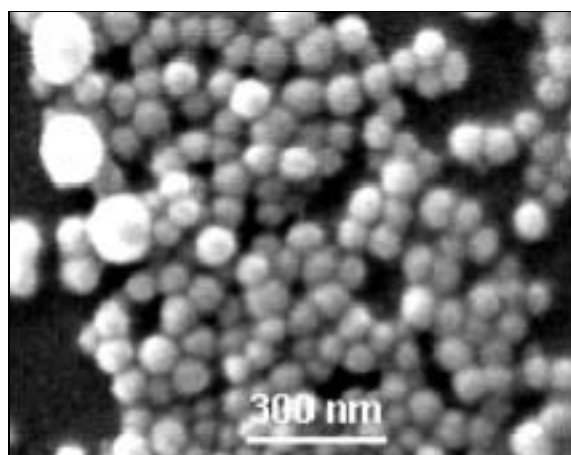
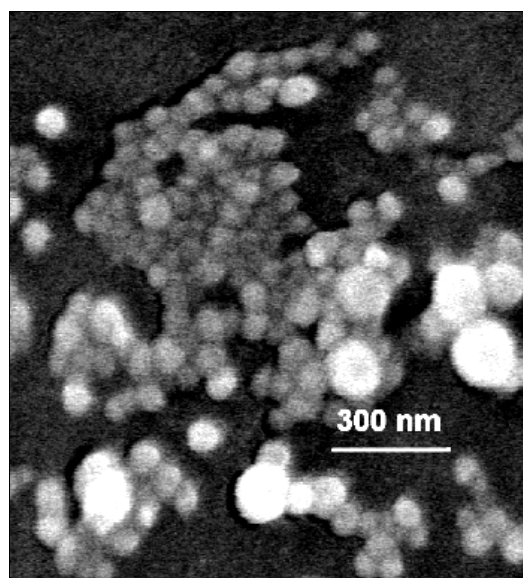


Fig. 8. SEM micrographs of a drop of 20 μm latex solution dried on glass substrate at room temperature after the preparation of polymer latex (*a*) and after three-month storing of the polymer latex at room temperature (*b*).

Table 2. Colloidal Parameters of Polymer Particles Prepared by the AIBN-Initiated Emulsion Polymerization Characterized by SEM

Sample	$\frac{D_n}{\text{nm}}$	$\frac{D_m}{\text{nm}}$	PDI	$\frac{D_v}{\text{nm}}$	$\frac{c_{\text{disp}}^a}{\text{mm}^3}$	Conditions
1	68.2	68.68	1.008	57.8	80	Dried in air
2	45.1	52.7	1.17	54.6	200	Dried in air
2'	50.1	80	1.612	60	200	Dried in air (the same conditions as for sample 2 but after three-month aging, Fig. 8b)
3	64.8	124.8	1.926	72.8	20	Spin coating
4	64.48	96.15	1.52	96.35	100	Dialysis, spin coating

**Fig. 9.** SEM micrograph of a drop of 20 μm latex solution dried on glass substrate by spin coating.**Fig. 10.** SEM micrograph of a drop of 20 μm latex solution (after dialysis) dried on glass substrate by spin coating.

the polydispersity index of the assembled polymer particles increases. The decreased amount of emulsifier in the particle surface layer is supposed to decrease the interpenetration of particle surface layers and so the formation of organized particle monolayers.

The sterically stabilized polystyrene nanoparticles with the particle size $D_n = 45$ nm (Fig. 8a) were formed by the emulsion polymerization of styrene initiated by AIBN (1×10^{-3} mol dm $^{-3}$) at the very large mass ratio Tween 20/styrene, 2.5. Fig. 8a shows that the polymer particles are relatively monodisperse. This behaviour deviates from that observed in the classical emulsion polymerization where the coarse polymer particles with high polydispersity are formed [1]. It is very interesting to note that the deposition of the miniemulsion polymer latex leads to the appearance of regular hexagonal arrangement. The thick interfacial layer and/or multilayers of nonionic emulsifier (Tween 20) at the particle surface favour the arrangement of the polymer particles into the two-dimensional lattices with the hexagonal structure. The continuous interpenetration of PEO chains of neighbouring polymer particles during the drying process leads to the organized arrangement of polymer particles.

CONCLUSION

The sterically stabilized polymer particles were prepared by the emulsion polymerization of styrene initiated either by the water-soluble initiator ammonium peroxydisulfate or the oil-soluble initiator 2,2'-azobisisobutyronitrile. The APS-initiated emulsion polymerization is faster than the AIBN-initiated one. Besides, Interval 2 is missing in all systems. The presence of larger amount of emulsifier or microdroplets shifts the particle nucleation to higher conversion. The polymerization rate *vs.* conversion dependence was characterized by three rate intervals. The (ordered monolayer) hexagonal arrangement of polymer particles appears under the high emulsifier concentration or the large mass ratio emulsifier/monomer. The presence of partial charge at the particle surface and/or the loosely packed emulsifier layer disfavors the organized arrangement. The increased interpenetration of PEO chains of neighbouring polymer particles during the drying process favours the

organized arrangement of polymer particles within the monolayer. The sterically stabilized polymer particles (AIBN-initiated, without surface charge) are more monodisperse than the electrosterically stabilized polymer particles (APS-initiated, with the electrical double layer around the polymer particle).

Acknowledgements. This work was supported by the Slovak Grant Agency VEGA through the Grant No. 2/4008/04, Science and Technology Assistance Agency through the Grants No. APVT-51-021702, APVT-20-017304, and State Program ŠO 51/03R060003R0601.

REFERENCES

- Piirma, I. and Chang, M., *J. Polym. Sci., Polym. Chem. Ed.* 20, 489 (1982).
- Capek, I., Bartoň, J., Tuan, L. Q., Svoboda, S., and Novotný, V., *Makromol. Chem.* 188, 1723 (1987).
- Kissa, E., in *Surfactant Science Series, 20: Detergency – Theory and Technology*. (Cutler, W. G. and Kissa, E., Editors.) P. 193. Dekker, New York, 1987.
- Napper, D. H., *Polymeric Stabilization of Colloidal Dispersions*. Academic Press, London, 1983.
- Ottewill, R. H., *J. Colloid Interface Sci.* 58, 357 (1977).
- Murray, C. B., Kagan, C. R., and Bawendi, M. G., *Annu. Rev. Mater. Sci.* 30, 545 (2000).
- Stock, R. S. and Ray, W. H., *J. Polym. Sci., Polym. Phys. Ed.* 23, 1393 (1985).
- Chudej, J. and Capek, I., *Polymer* 43, 1681 (2002).
- Capek, I., Chudej, J., and Janíčková, S., *J. Polym. Sci.* 41, 804 (2003).
- Capek, I. and Chudej, J., *Polym. Bull.* 43, 417 (1999).
- Capek, I., *Macromol. Symp.* 179, 153 (2002).
- Capek, I. and Funke, W., *Makromol. Chem.* 191, 2549 (1990).
- Capek, I., Riza, M., and Akashi, M., *Makromol. Chem.* 193, 2843 (1992).
- Huang, S., Tsutsui, G., Sakane, H., Shingubara, S., and Takahagi, T., *J. Vac. Sci. Technol., B* 19, 2045 (2001).
- Asua, J. M., *Prog. Polym. Sci.* 27, 1283 (2002).
- Miller, C. M., Sudol, E. D., and Silebi, C. A., *Macromolecules* 28, 2772 (1995).
- Lin, S. Y., Capek, I., Hsu, T. J., and Chern, C. S., *J. Polym. Sci., Part A: Polym. Chem.* 37, 4422 (1999).