

## Polymeric particles prepared with fluorinated surfmer

A. Pich<sup>a,\*</sup>, S. Datta<sup>b</sup>, A. Musyanovych<sup>a</sup>, H.-J. P. Adler<sup>a</sup>, L. Engelbrecht<sup>c</sup>

<sup>a</sup>*Institute of Macromolecular Chemistry and Textile Chemistry, Dresden University of Technology, D-01062 Dresden, Germany*

<sup>b</sup>*Indian Institute of Technology, Delhi, India*

<sup>c</sup>*EFKA Additives, The Netherlands*

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### Abstract

Fluoro-containing particles have been obtained by miniemulsion polymerization of styrene and *n*-butyl methacrylate in presence of fluorinated monomer mono-fluoroalkyl maleate (MFM) which acts as a surfmer providing efficient stability to obtained dispersion and functionalization of particle surface with fluoro-groups. Increase of the MFM concentration in reaction mixture reduces the particle size and dispersions with narrower particle size distribution can be obtained. Blends of fluorinated latexes with styrene–butadiene copolymer latex were examined with regard to formation of low free energy surfaces. It has been shown that blends containing MFM-functionalized polymeric particles possess more hydrophobic surfaces than similar latex films, where particles prepared by polymerization of expensive fluorinated monomer have been applied.

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### 1. Introduction

Fluorine-containing polymers have been proven to be an interesting class of materials with remarkable properties, including low surface energies, low dielectric constants and refractive indices [1], high chemical and thermal stabilities, and solubility in supercritical CO<sub>2</sub> [2]. The production of dispersions from fluoro-containing polymers is one possible way to overcome problems connected with difficult handling and poor solubility in common inexpensive solvents. The easiest pathway to preparation of fluorinated particles is polymerization of fluorinated monomers by heterophase polymerization process. Some efforts have been made in applying emulsion polymerization technique for the polymerization of fluoroacrylates [3]. In this case, high monomer conversion and sufficient dispersion stability were achieved after addition of acetone to water phase. Addition of organic solvent improves the monomer transport from the monomer droplets to growing particles,

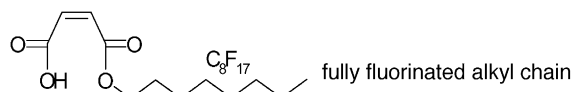
and this method is frequently used in industrial formulations using fluorinated monomers.

Another interesting technique for polymerization of fluorinated monomers is the miniemulsion polymerization. During miniemulsion polymerization small monomer droplets formed by shearing the system are polymerized by droplet nucleation mechanism so monomer diffusion through the water phase does not play a major role in reaction mechanism. Thomas et al., [4] reported synthesis of fluorinated particles by copolymerization of fluorine-containing acrylates with *n*-butylacrylate by means of miniemulsion polymerization. Similar polymerization technique was used by Landfester et al., [5] and polymeric particles with core-shell morphology have been obtained by copolymerization of fluorinated acrylates with styrene or methyl methacrylate.

The aim of the present study was preparation of fluorinated polymeric particles by using fluorinated surfactant containing polymerizable double bond (surfmer). This substance belongs to the class of reactive surfactants which have been successfully applied in heterophase polymerisation. Reactive surfactants can take part directly in the radical polymerisation process as polymerizable surfactants

\* Corresponding author. Tel.: +49 (0351) 46333858; fax: +49 (0351) 46337122

E-mail address: [andrij.pich@chemie.tu-dresden.de](mailto:andrij.pich@chemie.tu-dresden.de) (A. Pich).



Scheme 1. Chemical structure of MFM.

(surfmers, [6–10]), as transfer agents (transurfs, [11–16]) or as initiators (inisurfs, [17–22]). Finally such a surfactant is bond covalently to the particle providing the stability of the dispersion and functionalization of the particle surface. By using fluorinated surfmer one can expect that it can be applied both in emulsion polymerization and miniemulsion polymerization techniques in combination with other conventional acrylic monomers or styrene derivatives. Additionally, the stabilization of colloidal system and functionalization of particle surface with fluoro-groups can be achieved. Proposed approach gives a possibility to locate fluoro groups on the particle surface and not in the bulk polymer, so the amount of fluorinated monomer can be reduced to minimal value without any strong change of material properties. The fluorinated surfactant which we have used in this study is a fluoroalkyl maleate. This cheap commercial product which can be produced on large scale, so the low cost of raw materials, simple preparation method can make obtained polymeric nano-particles with fluorinated surface interesting for academic research and different industrial applications.

## 2. Experimental

### 2.1. Materials

Styrene (ST) (Merck) and *n*-Butyl methacrylate (*n*-BMA) (Aldrich, 99%) were distilled under reduced pressure before use and kept in refrigerator at  $-20\text{ }^{\circ}\text{C}$  without exposure to light. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (FL) (Aldrich) was used after appropriate purification procedure. MFM ( $M \approx 573$  [g/mol]) is the fluorinated product obtained from EFKA Additives and was used as received (Scheme 1).

Initiator 2,2'-azobisisobutyronitrile (AIBN) (Acros Organics, 98%) was used without any additional cleaning. Hexadecane (HD) (Aldrich, 99%) was used as received as hydrophobe. For the neutralisation of MFM, NaOH (Baker, 97%) was used as received. As conventional surfactant sodium dodecyl sulphate (SDS) (Merck, 99%) was used as received. Deionized water was used as polymerization medium. BSL dispersion (styrene-butadiene copolymer) was obtained from DOW Chemicals and used as received.

### 2.2. Synthesis of dispersions

#### 2.2.1. MFM-containing dispersions

MFM and NaOH were taken in 1:1 molar ratio and added to distilled water (to 100 ml water 5 g of MFM was added).

The mixture was then stirred at room temperature until all the solid MFM disappeared. Monomer (15 g), hydrophobe (0.625 g), and the initiator (0.4 g) were mixed together and then added to the MFM solution in water (160 g) and stirred for at least 30 min. The MFM concentrations in water were adjusted to 0.0095 mol/l; 0.0180 mol/l; 0.257 mol/l; and 0.0328 mol/l. The whole mixture was then sonified to make the miniemulsion for 3 min at 50% amplitude (Branson sonifier W450 Digital). Ice was placed around the reaction mixture to avoid overheating. All the reactions were carried out at  $70\text{ }^{\circ}\text{C}$ .

Polymeric particles obtained by polymerisation of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (FL), ST, and *n*-BMA stabilized with SDS were prepared in similar way.

### 2.3. Preparation of films

Mixtures of BSL-latex and fluorinated latex contain 10 wt%; 30 wt%; and 50 wt% of fluorinated particles in total polymer mixture. Latexes were mixed with magnetic stirrer overnight and formed bubbles were removed. Blends were made on previously cleaned glass plates with rakel (700  $\mu\text{m}$ ) and dried on the air for 48 h. Additionally, some blends were thermally cured in an oven at  $60\text{ }^{\circ}\text{C}$ .

### 2.4. Characterization methods

#### 2.4.1. Particle size analysis

The dynamic light scattering measurements were performed with DLS 700 (Otsuka, Japan) at different scattering angles. In dynamic LS, the Laplace inversion of a measured intensity-time correlation function  $G^{(2)}(t, q)$  in the self-beating mode can result in a line-width distribution  $G(\Gamma)$  [10]. For a pure diffusive relaxation,  $\Gamma$  is related to the translational diffusion coefficient  $D$  by  $\Gamma/q^2 = D$  at  $q \rightarrow 0$  and  $c \rightarrow 0$ , or a hydrodynamic radius  $R_h$  by  $R_h = k_B T / (6\pi\eta D)$  with  $k_B$ ,  $T$  and  $\eta$  being the Boltzmann constant, absolute temperature, and solvent viscosity, respectively. Typically, five measurements were performed for determination of hydrodynamic radius. Accuracy of measurements for hydrodynamic radius is  $\pm 3\%$ .

#### 2.4.2. Surface tension measurements

Surface tension measurements were made with Krüss Tensiometer (Wilhelmy method) at  $20\text{ }^{\circ}\text{C}$ . Appropriate solutions with different MFM concentrations were prepared and measurements were performed at least 24 h after preparation of solutions.

#### 2.4.3. Differential scanning calorimetry

DSC measurements were made with Mettler TA 4000 instrument. Before measurement samples were dried in vacuum for ca. 48 h. Samples were analyzed in closed aluminium cups. Measurements were made at heating rate  $5\text{ }^{\circ}\text{C}/\text{min}$  in nitrogen atmosphere.

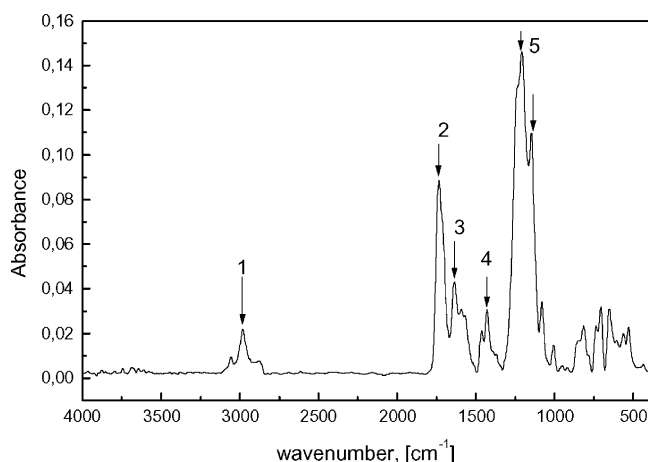


Fig. 1. IR spectrum of MFM.

#### 2.4.4. Scanning electron microscopy

SEM images were taken with Gemini microscope (Zeiss, Germany). Samples were prepared in the following manner. Dispersions were diluted with deionized water, dropped onto aluminium support and dried at room temperature. Prior to measurements particles were coated with conducting layer to improve the contrast. Pictures were taken at voltage of 4 kV.

#### 2.4.5. Atomic force microscopy

Measurements were made with Dimension 3100 (Digital Instruments Inc.) using the tapping mode regime (set point ratio, 90%; integral gain, 0.2; proportional gain, 2.0; amplitude set-point, 0.7 V; scan rate 0.901 Hz). Samples were prepared by spin coating technique (2000 rpm, 10 min) on previously cleaned glass supports.

#### 2.4.6. IR-Spectroscopy

IR spectra were recorded with Mattson Instruments Research Series 1 FTIR spectrometer. Dried polymer samples were mixed with KBr and pressed to form a tablet.

#### 2.4.7. Drop shape analysis

Contact angle was measured by drop shape analysis method by Krüss G10 instrument. Measurements were made on thoroughly dried films on glass plates by using deionised water as probe liquid. Advancing contact angles were determined by expanding the droplet on the surface until the equilibrium angle was observed. Receding angles were obtained by removing liquid from the droplet until its base contracted and an equilibrium angle was seen.

#### 2.4.8. Micro-hardness measurements

Measurements were performed with Fischerscope H 100 W Micro Hardness Control. Mixtures of polymeric dispersions were deposited on previously cleaned glass plates and dried on the air at room temperature for 48 h. Obtained polymer films (thickness ca. 0.2 mm) were used directly for measurements of hardness.

### 3. Results and discussion

#### 3.1. Fluorinated surfactant

Surfactants with fluorinated hydrophobic groups are a class of compounds in which there is growing interest because of their specific properties in a wide variety of applications and they show high interfacial activity. Under specific cases they can exhibit some special properties such

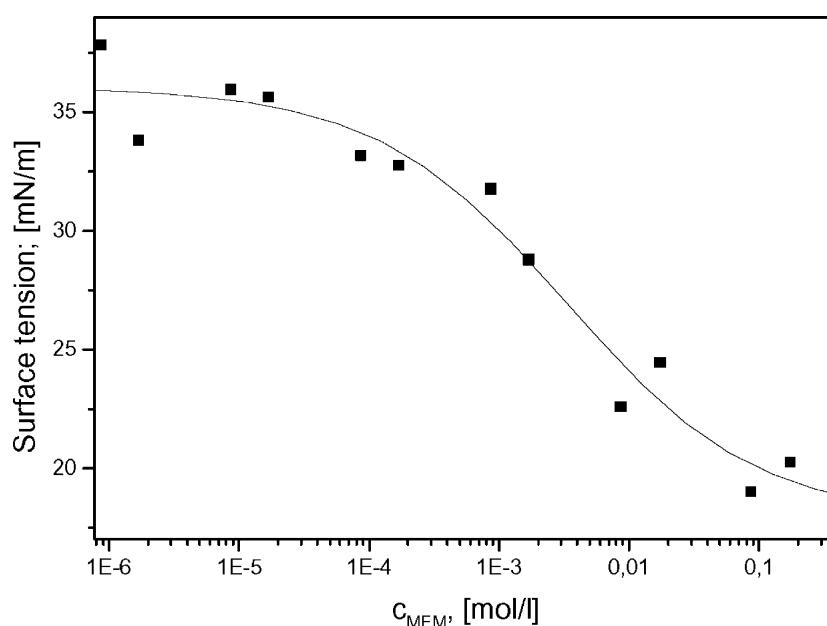


Fig. 2. Surface tension vs. concentration curve of MFM in water.

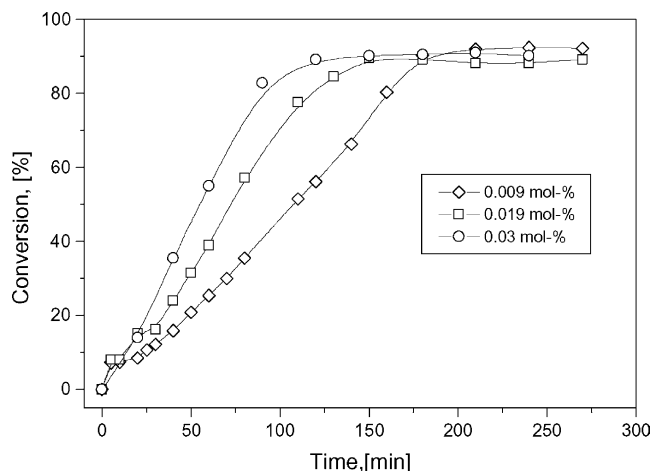


Fig. 3. Conversion-time curves of styrene polymerization at different.

as fire extinguishing property, lubricating property etc. [23]. The IR-spectrum of mono-fluoroalkyl maleate (MFM) is presented in Fig. 1. The strongest signals correspond to  $\text{CF}_2$  and  $\text{CF}_3$  groups ( $1370.37 \text{ cm}^{-1}$  and  $1208.13 \text{ cm}^{-1}$ ) (position 5) and carbonyl groups ( $\text{C}=\text{O}$ ) ( $1735.1 \text{ cm}^{-1}$ ) (position 2). Other important signals assigned in spectrum are aliphatic  $\text{CH}_2$  and  $\text{CH}_3$  groups vibrations at  $2981.56 \text{ cm}^{-1}$  and  $1463.58 \text{ cm}^{-1}$  (position 1 and 4, respectively) and  $\text{C}=\text{C}$  double bond signal at  $1636.44 \text{ cm}^{-1}$  (position 3).

MFM can be dissolved in water after neutralization of carboxylic group with sodium hydroxide. It has been found that presence of MFM molecules reduces surface tension of water solutions. Dependency of surface tension on MFM concentration in water is presented in Fig. 2.

It can be seen readily that MFM shows the characteristic behaviour of a surfactant; the surface tension decreasing with increasing concentration of MFM. However, unlike the

other surfactants, the surface tension value at very small MFM concentrations is around  $37 \text{ mN/m}$  which is considerably lower than the surface tension of pure water. This anomalous behaviour can be explained by the fact that MFM was an industrial product and not the pure one; so it might contain some other impurities which had some effect on the surface tension behaviour. Despite of this fact MFM shows regular trend in its surface tension behaviour with concentration, thus it can be concluded that MFM can be used as a fluorinated surfactant.

### 3.2. Miniemulsion polymerization in presence of MFM

In miniemulsion polymerization, the use of simple anionic surfactants is a most common case. However, other surfactants such as cationic and nonionic ones are also successfully used. One can expect that MFM, because of its unique structure, can act as an anionic fluorinated surfmer (combination of surfactant and co-monomer) in miniemulsion polymerization and fluorinated particles can be obtained. In the following work, two common monomers styrene and *n*-BMA were chosen for miniemulsion polymerization in presence of MFM. It is well known that the amount of surfactant in miniemulsion polymerization has an influence on the particle size and on the stability of the system. The concentration of MFM was varied in different formulations and the influence of MFM on particle size and solid content of the final latex was studied. It has already been established [4,5] that presence of hydrophobe in miniemulsion polymerization helps to stabilize the monomer droplets but the amount of hydrophobe in such formulations does not have much influence on the particle size and other parameters. So no investigation was carried out on the influence of the amount of hydrophobe and the

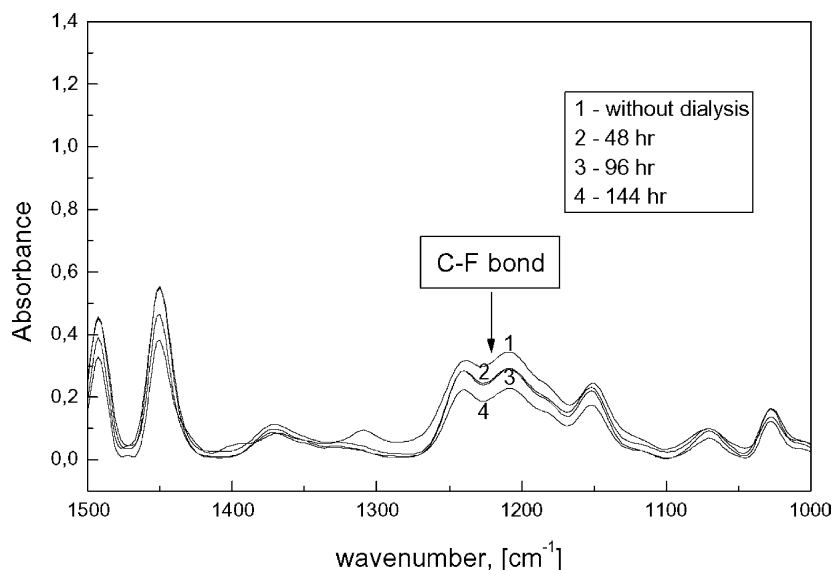


Fig. 4. Part of the IR spectra of PST/M latex (0.0328 mol/l MFM) before and after dialysis.

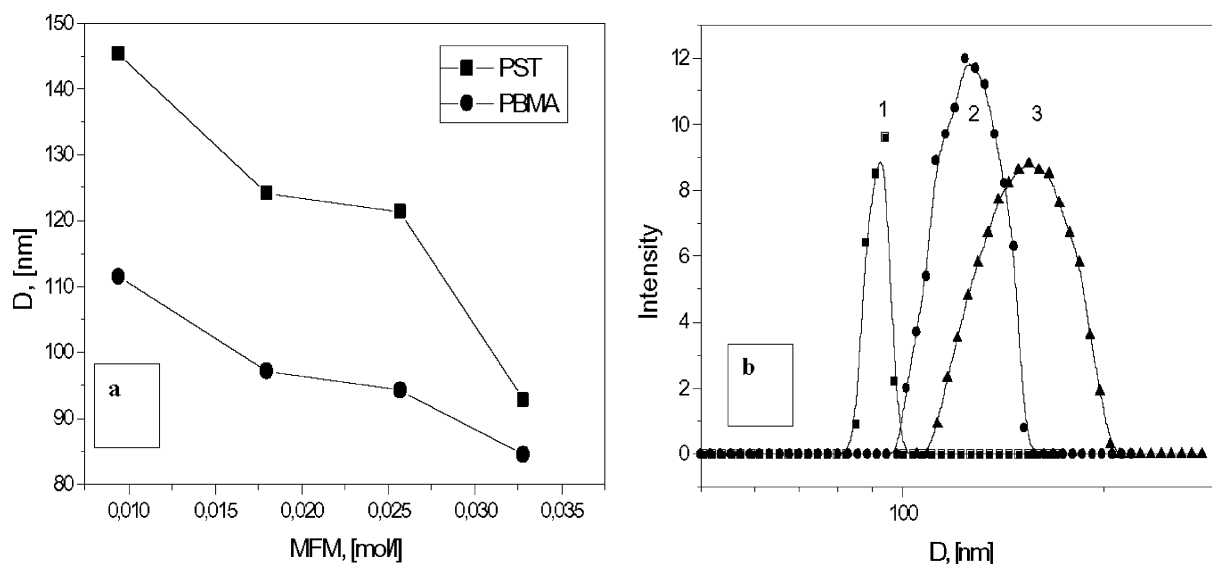


Fig. 5. Particle size as a function of MFM concentration (a); particle size distribution of PST particles prepared at different MFM concentrations 0.032 mol/l; 2–0.018 mol/l; 3–0.009 mol/l (b).

most commonly used hydrophobe hexadecane (0.625 g) was used in the same amount in each case.

From the kinetic study (Fig. 3), it is seen that with increase in MFM concentration the polymerization rate of styrene increases. Indeed increase in surfactant concentration increases the initial number of monomer droplets and consequently more droplets are initiated, hence the overall rate of polymerization increases [24].

Since MFM contains a double bond in its structure, there was a possibility that it may act as co-monomer during polymerization. To find out if MFM was reacting or not, the PST/M latex (polystyrene particles prepared with 0.0328 mol/l MOFAM) was dialysed for 7 days to see if MFM was physically bonded onto the particle surface or if it was chemically grafted. IR-spectra were recorded after certain time intervals and intensities of  $\text{CF}_2$ ,  $\text{CF}_3$  vibrations at  $1208\text{ cm}^{-1}$  which are characteristic to MFM were compared.

Table 1  
Latexes used for preparation of mixtures

N	Latex type	$D$ [nm]	$T_g$ [°C]
1	PST/S	101	95
2	PBMA/S	176	24
3	PFL/S	176	24
4	PFL/S	258.2	63.3
5	PST/M (0.009)	145.3	98.5
6	PST/M (0.0257)	121.3	99.4
7	PBMA/M (0.009)	111.53	25
8	PBMA/M (0.0257)	94.25	24.5
9	PBMA/M (0.0328)	84.5	23
10	BSL (matrix)	300	–50

S, SDS; M, MFM.

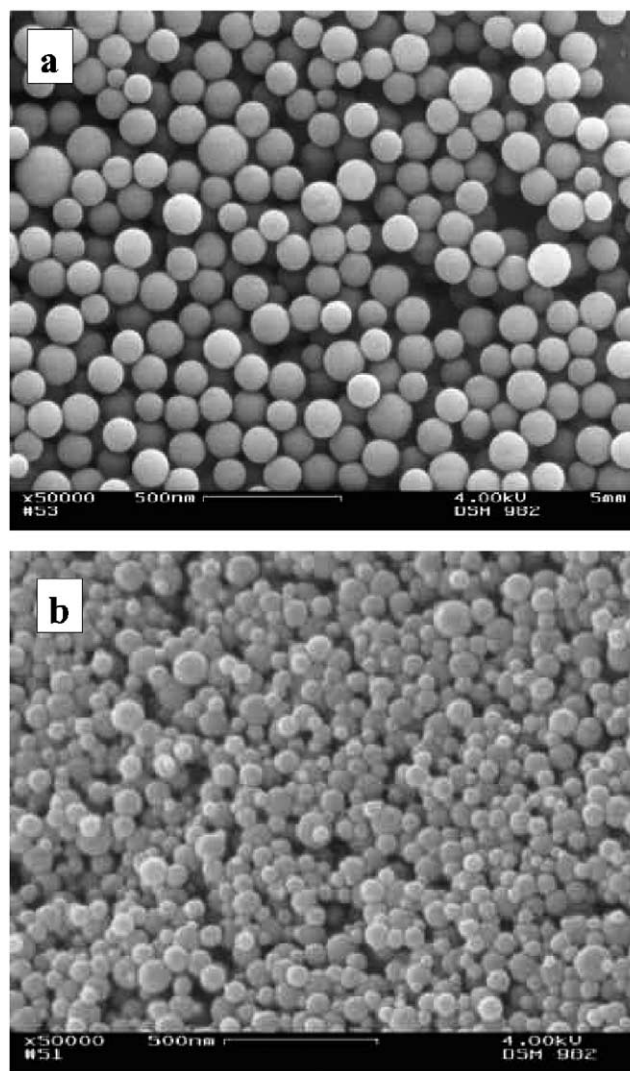


Fig. 6. SEM images of PST particles prepared at MFM concentrations: (a) 0.0090 mol/l; (b) 0.0180 mol/l.

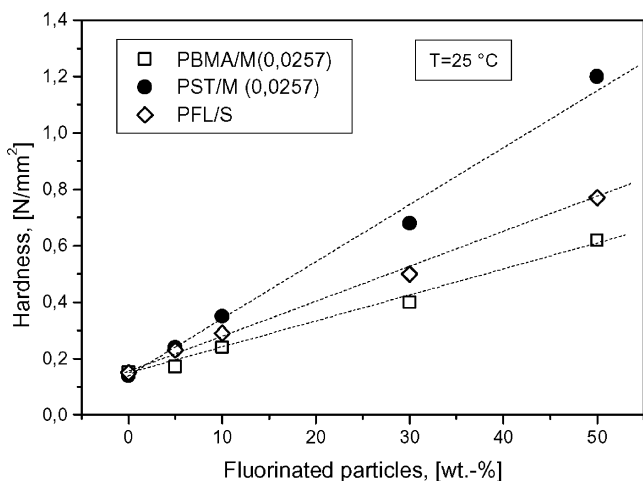


Fig. 7. Hardness of composite films as a function of different fluorinated particle content in BSL matrix.

It can be seen from Fig. 4 that the peak in this region had decreased only a little after dialysis but was not completely eliminated even after 144 h of dialysis. From this it can be concluded that MFM has reacted partially with styrene during the polymerization and thus chemically bonded to the latex particles. Approximately 8% of the total MFM amount used for polymerization has been removed by dialysis from the dispersion.

### 3.3. Characterization of fluorinated particles

Fig. 5(a) shows that the average particle size decreases with increasing MFM concentration. This trend is similar for poly(styrene) and poly(*n*-butyl methacrylate) particles. PST particles prepared with MFM are larger if to compare with PBMA particles prepared at similar MFM concentration. Smaller particle size of PBMA particles is the consequence of higher hydrophilicity of PBMA if to compare with poly(styrene). Therefore at similar reaction conditions acrylate system can increase overall surface area (or reduce particle size and increase particle number). However, it is clear from Fig. 5(a) that increasing of MFM content leads to more or less similar particle dimensions for both types of polymers.

Fig. 5(b) shows the distribution of particle size for PST particles prepared at different MFM concentration. It can be seen that particle size distribution becomes narrower when larger MFM amounts are applied in polymerization process.

SEM images of PST particles are shown in Fig. 6. It is evident that at lower MFM concentration particles are larger, but particle size distribution is quite broad. Increase of MFM concentration leads to more uniform particle size distribution and decrease of particle dimensions. Microscopy images correlate with light scattering measurements presented above.

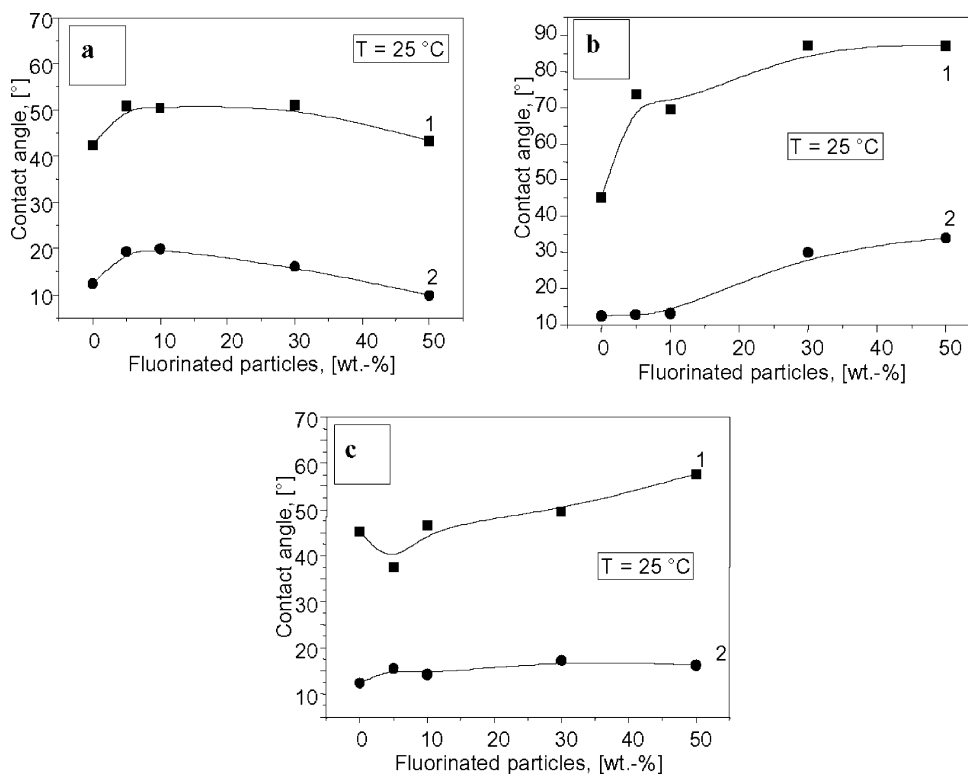


Fig. 8. Contact angle measurements of composite films prepared with different fillers: (a) PST/S, (b) PST/M (0.0257 mol/l), and (c) PFL/S (1, 2—advancing and receding contact angles, respectively).



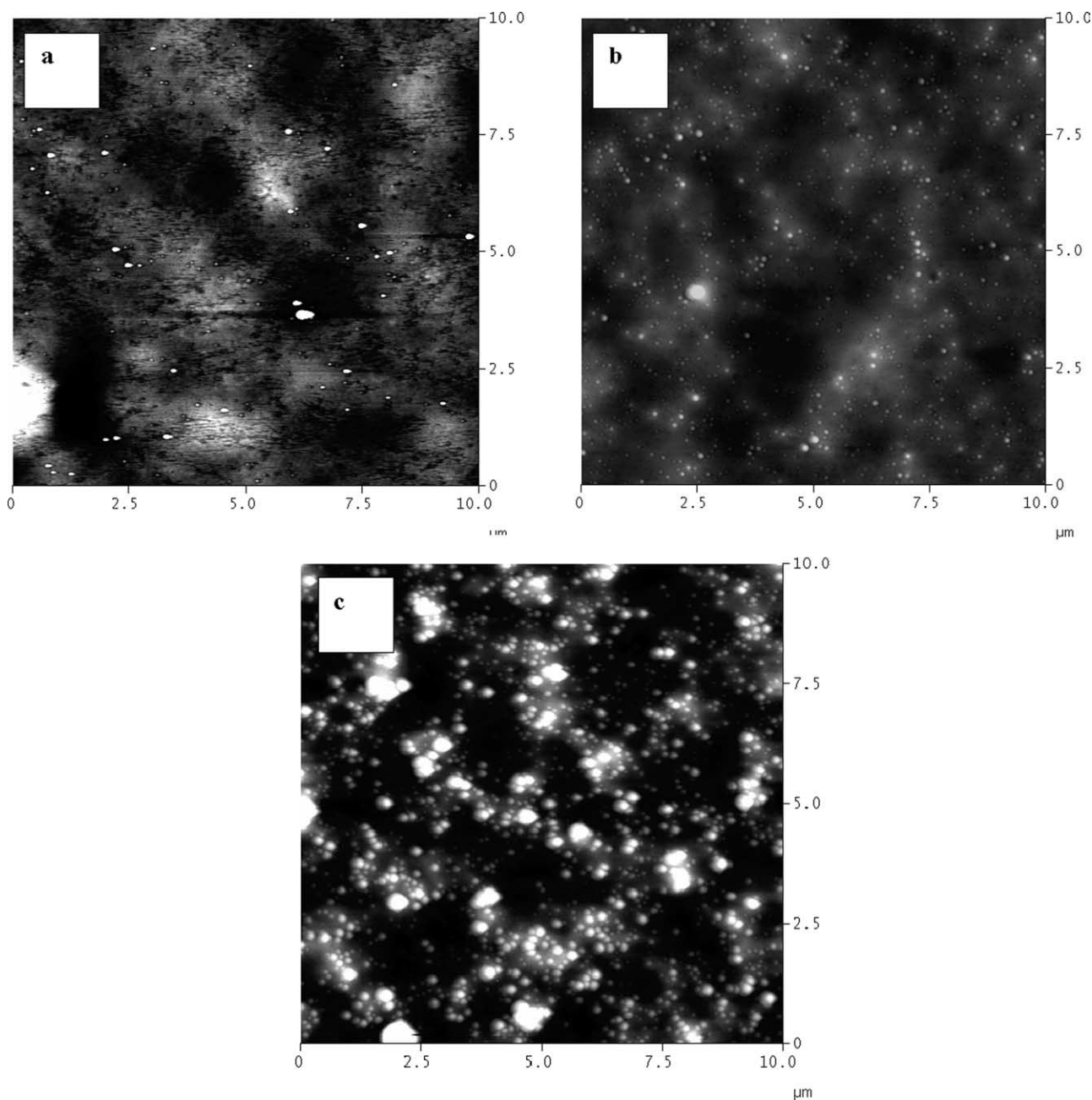


Fig. 9. AFM height images of composite films prepared with 10 wt% (a), 30 wt% (b), and 50 wt% (c) of PST/M particles (the height scale is 0–100 nm for images (a), (b) and 0–20 nm for image (c)).

### 3.4. Properties of composite films

PST and PBMA particles prepared in presence of MFM (PST/M and PBMA/M, respectively), as well as their fluorine-free analogues where SDS was used as a stabilizer (PST/S and PBMA/S) were mixed with fluorine-free film-forming matrix (low- $T_g$  BSL latex consisting of styrene-butadiene copolymer). Particles prepared by polymerization of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl methacrylate (FL) and stabilized by SDS have been used for comparison purpose. Table 1 presents most important

characteristics of dispersions which have been used in this study.

Composite films were investigated by different analytical methods. Fig. 7 presents results of micro-hardness measurements performed with films dried at room temperature.

Results presented in Fig. 7 indicate that addition of different fillers to BSL latex increases film hardness to different extent. This effect is quite clear if to consider  $T_g$  values for BSL matrix and different fluorinated particles. The  $T_g$  values for fluorinated additives are quite higher as that of BSL matrix and the glass transition temperature

decreases in following range PST/M, PFL/S, and PBMA/M. Therefore, addition of harder fluorinated particles should increase hardness of the composite material. This behaviour is actually observed in Fig. 7 and the hardness of latex films increases nearly in linear order with increasing fluorinated filler particle content.

Some selected contact angle measurements are presented in Fig. 8. Contact angles of composite films prepared with PST/S sample (Fig. 8(a)) are not dependent on PST/S content and maximal contact angle reached in this case was 52°.

When PFL/S particles have been used for preparation of composite films the contact angle increases with increasing PFL/S amount (Fig. 8(c)). But the contact angle value measured for latex film containing 50 wt% of FL is 60°, what is not much higher than blends with fluorine-free PST/S sample. Quite different behaviour was observed when PST/M (0.0257 mol/l) particles were used in composite films (Fig. 8(b)). In this case, the contact angle increases with PST/M content in the mixture and reaches maximum 90°, which is a considerable improvement of the surface hydrophobicity.

Composite films prepared with PST/M particles have been investigated with AFM. Fig. 9 presents the microscopy images of film surfaces.

AFM investigations indicate that, amount of hard PST/M particles on the film surface increases with increasing PST/M amount in the mixtures. This is probably the reason for increase of contact angle which was discussed previously. Since MFM molecules are attached to the polystyrene particle surface, they will be also present on the surface of composite films. It is also obvious that if the PST/M amount in the mixtures increases the tendency to particle agglomeration is stronger. Films prepared at 50 wt% of PST/M exhibit large domains and filler particles are not homogeneously distributed on the surface. Similar effects were detected in case when PBMA/M dispersions were used to prepare composite films with BSL dispersions. Measured contact angles of composite films were comparable to that of PST/M-filled films. For this reason, these results are not discussed in details here.

#### 4. Conclusions

Fluorinated monomer mono-fluoroalkyl maleate (MFM) has been successfully used as a surfmer in miniemulsion polymerization of styrene and *n*-butyl methacrylate. It has been demonstrated that the final size and particle size distribution of fluoro-containing nano-particles can be controlled by concentration of MFM in reaction mixture. Obtained fluoro-containing particles can be easily mixed

with styrene–butadiene copolymer latex to form composite films. Contact angle measurements indicate that surface of such films has more hydrophobic character if to compare with pure styrene–butadiene latex and contact angle increases when amount of fluorinated particles is raising up. Microscopy investigations indicate that certain fraction of fluorinated particles can migrate to the film surface during drying process providing hydrophobic properties to the composite layer.

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