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ORIGINAL CONTRIBUTION

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Surface morphology of polypyrrole core/polyacrolein shell latex by atomic force microscopy (AFM)

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Abstract Polypyrrole latex (P(P)), synthesized in Redox polymerization of pyrrole, was used as seed for radical polymerization of acrolein initiated with $K_2S_2O_8$. In this process the polypyrrole core/polyacrolein shell latex (P(P–A)) was obtained. Morphology of the surface of P(P–A) particles was investigated by atomic force microscopy (AFM). It was found that macromolecules of polyacrolein are not randomly distributed on the surface of polypyrrole but form patches. Apparently, attraction between macromolecules of polyacrolein in the surface layer is high and the enthalpy of formation of polyacrolein macromolecule clusters is sufficient to compensate, at least, the negative entropy change due to ordering of these macromolecules. Thickness of the polyacrolein layer on the surface of polypyrrole particles, which were covered only partially with polyacrolein, was equal to only 1.6 nm (standard deviation $\sigma =$ 0.2 nm) and thus, it was reasonable to assume that it corresponded to the monolayer coverage.

Key words Atomic force microscopy – core-shell latex – polypyrrole – polyacrolein – surface morphology

Introduction

Seeded emulsion and/or dispersion polymerizations are used for synthesis of homopolymer latexes with a narrow particle diameter polydispersity and for latexes with core–shell morphology with core and shell composed of different polymers [1–9]. Depending on the actual system (nature of seed latex and monomer, mode of monomer addition, initiator, and reaction medium) propagation proceeds in seed particles swollen with a second monomer, or is initiated in solution from which the growing macromolecules precipitate, when their chain length exceeds the critical one, and may be adsorbed onto the seed particles [1, 6, 10]. In the case when this adsorption is thermodynamically unfavorable, or kinetically hampered, new particles are nucleated and when such particles do not coalesce with the primary ones this step of polymerization yields the mixture of two homopolymer latexes. Regardless of the actual mechanism of particle formation, once the outer shells are created, they also could be swollen with a monomer, providing the new environment for propagation.

In principle, there are two possibilities for the initial stage of shell formation by adsorption of macromolecules of a second polymer (with still propagating or with terminated active centers). These macromolecules could be adsorbed: (i) randomly onto the surface of the seed support, (ii) or in a way leading to clusters covering densely only fragments of seed particles. In the former case, the surface of seed latex would be gradually modified during polymerization, whereas in the latter, it would be composed of the covered and free patches. Still very little is known on the arrangement of polymer macromolecules during initial stage of their adsorption. However, there are some indirect evidences suggesting formation of the patched structures in the case of adsorption of protein macromolecules [11–13].

Recently, we reported on synthesis of polypyrrole core/polyacrolein shell latex (P(P–A)) by radical polymerization of acrolein carried out in presence of the polypyrrole seeds [14]. The polypyrrole seed particles, obtained earlier in the Redox polymerization, were positively charged. Macromolecules of polyacrolein, formed in radical polymerization initiated with $K_2S_2O_8$, were equipped with negatively charged sulfate end groups, resulting from the incorporation of initiating radical anions. Electrostatic interactions facilitate adsorption of polyacrolein macromolecules onto the surface of polypyrrole support. However, during this process the positive charge of the polypyrrole core particles steadily decreases. Consequently, the amount of polyacrolein which could be attached to polypyrrole seeds is limited because, at the moment of full compensation of the positive charge of polypyrrole seeds with the negative charge of the polyacrolein shell, the core–shell particles lose their electrostatic stabilization, aggregate, and precipitate from suspension [14]. Therefore, the P(P–A) latexes forming stable suspensions are interesting as model particles with limited thickness of the shell. In this paper, we describe our observations of surfaces of P(P–A) particles by atomic force microscopy (AFM). We expected that, for this system, it will be possible to discriminate between the two conceivable modes of adsorption of polyacrolein macromolecules, namely, the random one and the adsorption with the formation of polyacrolein patches.

Atomic force microscopy was used for imaging various objects of molecular and supramolecular dimensions, in particular, dendrimers [15], polymeric gels [16], and latexes [17–22]. Studies were carried out in the contact and tapping modes. Whereas maximal resolution (in the x, y plane) of imaging in the tapping mode is usually lower than in the contact mode, the latter method is not well suited for the study of particles which are loosely attached to the support, and often introduces artifacts. These artifacts are usually due to friction between a tip and an imaged surface, in extreme cases resulting in displacement of investigated objects [18, 21].

Experimental part

Polypyrrole core/polyacrolein shell latex was synthesized as it was described in our earlier paper [14]. Here we will recall only briefly the synthetic procedure. Polypyrrole seed latex (P(P)) was synthesized in Redox reaction between pyrrole and $FeCl_3 \cdot 6H_2O$ according to the recipe described earlier by Armes et al. [23]. Subsequent synthesis of a polyacrolein shell was carried out by polymerizing 0.2 ml of acrolein in the presence of 0.6 g of polypyrrole. Mass median diameters and geometric standard deviations (GSD) of log-normal distributions of diameters of P(P) seeds and of P(P–A) core-shell latex particles, determined by dynamic light scattering, were equal to $D_M(\mathrm{P}) = 121$ nm, GSD = 1.2 and $D_M(\mathrm{P{-}A}) = 148$ nm, GSD = 1.3 for P(P) latex and for P(P–A) core–shell particles, respectively. Surface charge of P(P) seed particles, determined conductometrically, was equal to 91 $\mathrm{mC/m^2}$ and decreased upon formation of the polyacrolein shell to 45 $\mathrm{mC/m^2}$.

For observations by atomic force microscopy, the positively charged P(P) latex was adsorbed onto quartz slides, which after treatment with KOH had negative $\equiv\mathrm{SiO^-}$ groups at the surface and, thus, provided better attachment of latex particles. This approach decreased difficulties in observations, due to the adventitious displacement of particles with the AFM tip. The P(P–A) particles were immobilized covalently on the surface of quartz slides modified with γ-aminopropyltriethoxysilane [24]. Details of such immobilization are described in our earlier papers [25, 26]. After immobilization, only these fragments of the surfaces of latex particles which were in contact with quartz, and thus invisible for AFM observations, were changed, leaving the whole remaining parts not altered. Covalent immobilization allowed easy observation of large number of P(P–A) particles providing information on their size and surface morphology. For AFM observations we used a Nanoscope III apparatus (Digital Instruments) in the tapping mode (resonant mode with an intermittent contact) with Si cantilever oscillated at 350 kHz with an amplitude about 50 nm. The curvature radius of the tips used in our experiments were 7 ± 2 nm. None of the pictures was treated with any computer filtering procedures. In case of the presented "side views" we have chosen arbitrarily only the view angle.

Results and discussion

The typical AFM picture of the polypyrrole seed particle is shown in Fig. 1. Due to vertical probing by the AFM, only the upper part of the particle is properly visualized and this spherical object looks like a distorted hemisphere. Surface of all monitored P(P) seeds was smooth, like the one illustrated in Fig. 1. An example of the AFM picture of P(P–A) particles is shown in Fig. 2. Even a brief comparison of the AFM picture of the P(P) seed (cf. Fig. 1) with the

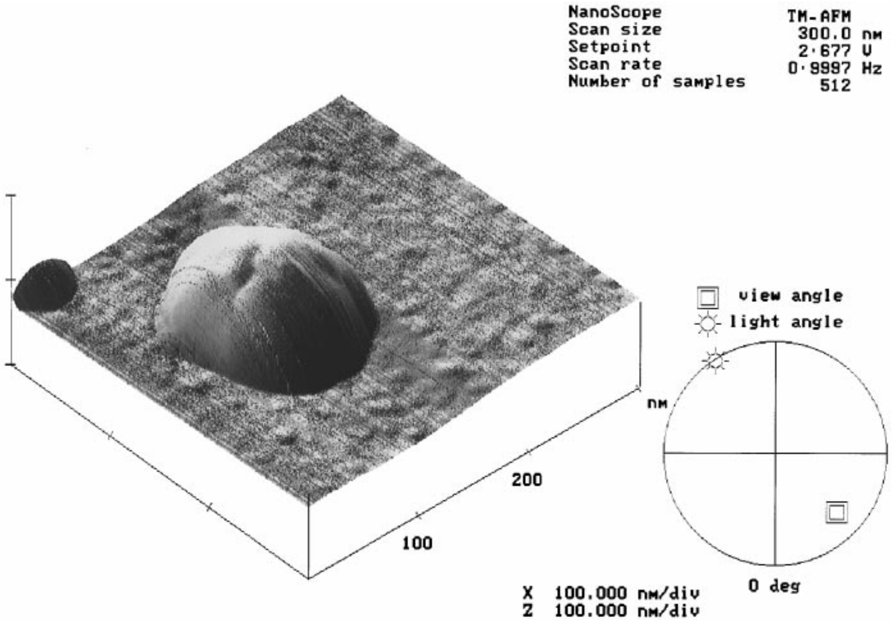

Fig. 1 AFM picture of P(P) latex particle on quartz

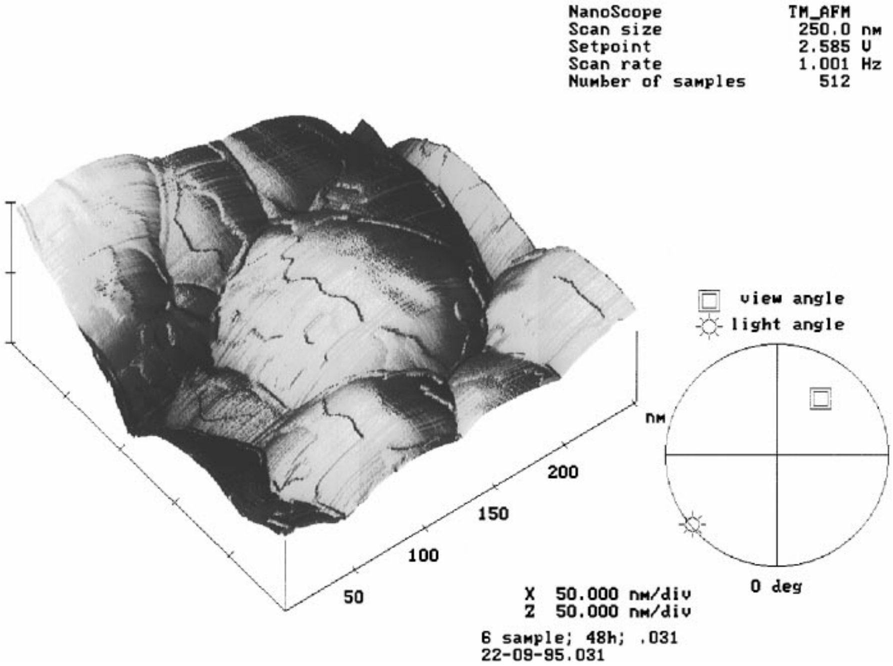

Fig. 2 AFM picture of an aggregate of P(P–A) particles immobilized on quartz

picture of P(P–A) particles (cf. Fig. 2) indicates a clear difference in morphology of their surfaces. Surface of the P(P–A) particles is unevenly coated with polyacrolein, forming patchy structures. Analysis of cross sections of 20 P(P–A) particles (an example is shown in Fig. 3) allowed us to measure thickness of these layers which was found equal to 1.6 ± 0.2 nm.

It is always a question whether measurements of heights of various objects by AFM provide real values. During imaging of fine particles and proteins in the constant force mode, Nagayama et al. [21] noticed artifacts (particles were not clearly identified) which were related to some shear forces between the probe and a surface of an object. In our studies we used a tapping mode. In these experiments a cantilever and a tip oscillate close to the cantilever's resonant frequency (ca. 350 kHz). The oscillating tip approaches a sample to a distance when it begins to strike the studied surface, which leads to a small reduction

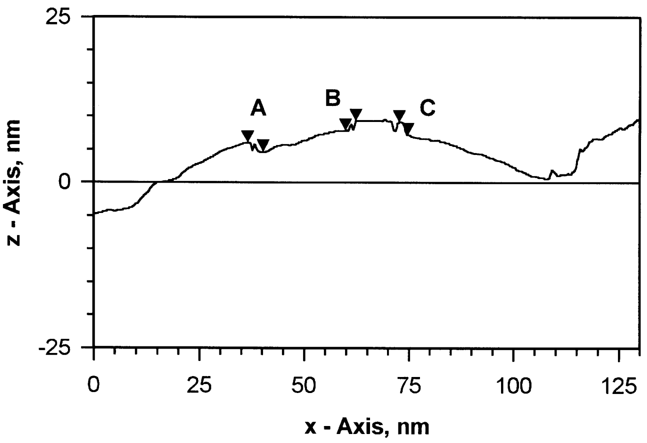

Fig. 3 An example of the "cross section" of a fragment of P(P–A) particle reconstructed from the AFM image. Vertical distance between the pointers equals to 1.39 nm (A), 1.51 nm (B) and 1.97 nm (C)

of the amplitude of oscillations. The vertical position of the sample is adjusted by a feedback system to maintain the preset amplitude of oscillations. Registration of the vertical position of the sample during scanning is used as a basis for computer-generated picture illustrating morphology of the surface of the sample. Any lateral and shear forces are eliminated in this type of imaging [22]. However, differences in the tip interactions with various areas of investigated surface still have to be taken into account. They are not important only when the surface is chemically uniform. To reduce the possible differences in the tip polypyrrole and tip polyacrolein interactions, we registered pictures at the conditions when differences between the amplitude of oscillations of the tip far from the surface and when the tip was engaged were minimal and at the same moment still allowed to obtain a stable picture. This makes us to believe that the measured thickness of the layers on the P(P–A) particles is close to the real one.

Difficulties in observations of P(P) seed particles weakly attached to the quartz did not allow to measure a sufficiently large number of objects and thus to determine their average diameters with the required accuracy. However, we did not notice particles with diameters smaller than 90 nm and larger than 130 nm.

Strong, covalent immobilization of P(P–A) particles onto the quartz slides eliminated complications in AFM observations allowing to measure diameters of more than 300 of particles on three different P(P–A) samples. Directly, on the basis of these measurements, we estimated that the number-average particle diameter was equal to D_n(P–A) = 114 ± 17 nm. Correction for the tip radius (7 ± 2 nm) gave D_n(P–A) = 100 ± 20 nm. This was significantly lower than the average diameter determined by dynamic light scattering which was equal to 148 nm. For the P(P) particles the dynamic light scattering gave value of the mediane-averaged diameter equal to 121 nm suggesting, therefore, that polyacrolein layer on the P(P–A) particles is ca 13.5 nm thick.

Simple calculations based on the ratio of the amount of acrolein, used for polymerization creating the shell, and the amount of polypyrrole in P(P) seeds constituting the core of P(P–A) particles allowed us to conclude whether the value of the thickness of polyacrolein layer (13.5 nm) which was found from the dynamic light scattering could be accepted as the genuine one.

Assuming that the analyzed particles are perfectly spherical, monodisperse, and have the ideal polypyrrole core/polyacrolein shell structure with a sharp boundary it was possible to obtain the following formula:

$$\frac{M_A}{M_P}\frac{d_P}{d_A} = 3\left(\frac{h}{R_P}\right) + 3\left(\frac{h}{R_P}\right)^2 + \left(\frac{h}{R_P}\right)^3 , \qquad (1)$$

where M_A and M_P denote masses of polyacrolein (assuming complete monomer conversion and full deposition onto polypyrrole seeds equal to mass of acrolein) and of polypyrrole seeds, respectively, $d_A = 1.35$ g/cm^3 and $d_P =$ 1.36 g/cm^3 are used for densities of polyacrolein and polypyrrole, R_P denotes the radius of P(P) seed particles and h the thickness of the polyacrolein shell. Remembering that the P(P–A) particles were obtained by polymerization of 0.2 ml of acrolein (0.168 g) added to 0.6 g of P(P) seeds it was possible to calculate h/R_P from Eq. (1). This ratio was found to be equal to 0.0856. Obviously, $h/(R_{P-A} - h)$, where R_{P-A} denotes the radius of the P(P–A) particles, is also equal to 0.0856.

For diameters of P(P–A) particles determined by AFM ($R_{P-A} = D_n$(P–A)/2 = 50 ± 10 nm), the thickness of the polyacrolein layer (calculated from the relation $h/(R_{P-A} - h) = 0.0856$) was calculated to be equal to $h = 4.0 \pm 0.8$ nm. Similar calculations based on the diameter of the polypyrrole seed particles determined by dynamic light scattering ($R_P = D_M$(P)/2 = 60 ± 10 nm) resulted in $h = 5.2 \pm 0.9$ nm, i.e. a value only slightly higher than that determined from AFM pictures. Thus, the thickness of polyacrolein layer evaluated as the difference of the radii of P(P–A) and P(P) particles measured by dynamic light scattering and equal 13.5 nm is unreasonably high and it is impossible to produce such thick layer from the amount of acrolein used for polymerization. The following reasons may contribute to the explanation of this observation. The dynamic light scattering measurements were performed for particles suspended in water in which the polyacrolein layer could be swollen and thus may be larger than for dry particles. Moreover, the hydrodynamic radii determined by dynamic light scattering also includes layers of adsorbed solvent and ion molecules, the latter especially in the case of charged particles. And, last but not the least, commercial software for treatment of dynamic light scattering data are written for homogeneous particles and any difference in values of refractive index coefficient along the particle radii would affect the correctness of the results.

It is important to note that the thickness of the polyacrolein layer observed in the cross-section pictures of P(P–A) particles (1.6 ± 0.2 nm) was lower than that estimated from mass of polyacrolein available for attachment to the surface of 0.6 g of the P(P) latex (4.0 ± 0.8 nm). Previously, we found that for 0.6 g of P(P) seeds, the polymerization of the amount of acrolein which was two times larger than that used for synthesis of P(P–A) particles investigated in this work, resulted in particle aggregation. Thus, it is reasonable to assume that during any particle work-up (e.g. purification by centrifugation, resuspension, and filtration) a fraction of particles predominantly with thicker polyacrolein layer could be lost. Moreover, estimates of the thickness of the very thin polyacrolein layer from the amount of P(P) seeds and the amount of acrolein used for polymerization were done with the assumption that density of polyacrolein in this layer is the same as for the polyacrolein in bulk. This assumption may be incorrect. Density of polyacrolein macromolecules in the layer with thickness close to that of monomolecular dimensions could be significantly higher than that for the corresponding bulk polymer. This is because macromolecules of polyacrolein, which are equipped with the negatively charged end groups, are expected to be better packed directly at the surface of P(P) particles, due to the electrostatic interactions with the positively charged polypyrrole support. Moreover, the degree of packing, and therefore the density, of polyacrolein in thin layer on P(P) particles could be increased because of the interfacial tension.

The formation of polyacrolein patches on the surface of polypyrrole seed particles conforms to the following mechanism. At the beginning of adsorption, the macromolecules of polyacrolein can move effectively at the surface of polypyrrole, either due to lateral diffusion or desorption and adsorption. At the moment when a few of them assemble into a cluster, this cluster becomes immobilized as a result of its higher mass, and its lateral diffusion and desorption would be reduced. Such clusters would act as centers nucleating further adsorption of polyacrolein macromolecules. However, these clusters should grow mostly laterally because the electrostatic attraction between polyacrolein and polypyrrole makes such adsorption relatively more efficient than the adsorption in subsequent layers when the positive charge of polypyrrole would be screened with the first layer of polyacrolein macromolecules with the negatively charged end groups. Formation of clusters is an entropically unfavorable process, like any other process leading to more ordered structures. Energy of interactions between macromolecules of polyacrolein with surface of polypyrrole latex particles is the same regardless whether the macromolecules are assembled into clusters or not. Therefore, we have to accept that the observed clustering results from the attraction between polyacrolein macromolecules in the surface layer, with enthalpy of these interactions sufficient to compensate the negative entropy change which has to occur during ordering of polyacrolein macromolecules. The model mentioned above is in agreement with computer simulation studies of the morphology of assemblies formed by adsorption and immobilization of interacting particles [27].

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