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Synthesis of Monodisperse Submicron Spherical Poly(methylmethacrylate) Particles and the Molecular Dynamics Simulation

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Abstract—The molecular-dynamics method has been used to determine the conformational states of poly(methyl methacrylate) chains in a medium composed of water and a monomer (methyl methacrylate). Experimentally detected spherical particles resulting from polymerization have been found to take the form of droplet-type aggregates containing several chains, with the water and monomer concentrations in the aggregates differing from those in the dispersion medium. It has been shown that the methyl methacrylate concentration in an initial reaction mixture of about 20% is optimal for the formation of spherical droplet-type aggregates. It has been experimentally established that spherical poly(methyl methacrylate) particles with a narrow size distribution are formed at a methyl-methacrylate concentration of ≈23%.

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INTRODUCTION

Under certain conditions, ordered structures having a period comparable with the optical wavelength may be assembled from submicron particles. In the scientific literature, these structures are commonly referred to as superlattices or photon crystals. The former designation indicates the large period of a cell as compared with ordinary crystals, while the latter one is related to their unique optical properties [1, 2].

The behavior of photons in these media is similar to the behavior of electrons in crystalline dielectrics and semiconductors. Therefore, the spectrum of electromagnetic waves in them has, similarly to the spectrum of electronic states in semiconductors, a band character, which gives the possibility of regulating the lifetime of exited atoms or molecules and localizing electromagnetic waves in lattice defects. This unique combination of light localization with control of radiation dynamics offers wide opportunities for practical use of photon crystals—from supersensitive sensors to optoelectronic systems.

Reproducible processes of production of photon crystals with perfect structures are necessary for their practical application. In practice, three-dimensional periodic materials can be formed by packing polymer spherical particles (of the same size) into regular structures during their deposition from dispersions. Therefore, production of particles with very narrow size distributions is an important experimental problem, because this is the main condition for the formation of defectless periodic structures [3, 4].

The conditions for the formation of spherical particles from methyl methacrylate (MMA) emulsified in water have been described in [5, 6]. Free-radical chain polymerization of MMA may be conventionally divided into three steps, i.e., the decomposition of a polymerization initiator into radicals—active sites of polymerization, the interaction of the monomer with the radicals followed by molecule chain propagation, and polymer-chain termination. MMA polymerization has been investigated in detail, while the mechanism for the formation of spherical particles from polymer chains remains to be studied. The molecular-dynamics method is most suitable for the investigation of this process. This method has successfully been used to simulate solutions and to study membranes containing poly(methyl methacrylate) (PMMA) [7].

CALCULATION METHOD

The molecular-dynamics method enables one to study the behavior of a single polymer chain or a group of polymer molecules in both a medium and vacuum. This method has been described in detail in a number of communications [8–13]. It was successfully applied to calculate the properties of various molecular compounds. The main stage of this method is the calculation of forces, which are found from the pattern of an interaction potential. The interaction potential is

Interaction-potential parameters

Atom pair	A_{ii}, Å^6 kcal/mol	B_{ii}, kcal/mol	C_{ii}, Å^{-1}	Reference
H–H	27.3	2654	3.74	[31]
C–C	568	83630	3.6	[31]
O–O	12762	96166	4.25	[32]

commonly represented as the sum of several terms [14]:

$$U = U_\mathrm{s} + U_\mathrm{b} + U_\mathrm{t} + U_\mathrm{VdW} + U_\mathrm{e},$$

that refer to the potential energies of valence bonds, U_s; valence angles, U_b; torsion angles, U_t; van der Waals interaction, U_VdW; and Coulomb forces, U_e.

PMMA has been investigated by the molecular-dynamics method in a number of works [7, 15–17]. The values of potential parameters U_s, U_b, U_t, and U_e for MMA have been presented in [15]. These parameters were used in our calculations.

The intermolecular interaction was described via atom–atom potentials [18]. This approach enables one to calculate the interaction of molecules based on the interactions between their atoms. Interatomic-interaction potential U_VdW was expressed as follows:

$$U_\mathrm{VdW} = \sum_{i,j}\left(\frac{-A_{ij}}{r_{ij}^6} + B_{ij}\exp^{(-c_{ij}r_{ij})}\right).$$

Coefficients reported in [19] were used for the U_VdW potential, as they were in our previous works [20–24]. Parameters of organic molecular crystals (lattice constants and vibration frequencies) and structures of liquid crystals calculated based on this potential were shown to be in good agreement with experimental data [20–24]. The molecular-dynamics method that we employed in this work was described in detail in the same publications. The interaction potential parameters used to calculate PMMA are listed in the table. The A_{ij}, B_{ij}, and C_{ij} cross values of the potential were found by the following formulas:

$$A_{ij} = \sqrt{A_{ii} + A_{jj}},\quad B_{ij} = \sqrt{B_{ii} + B_{jj}},\quad C_{ij} = (C_{ii} + C_{jj})/2.$$

The coordinates and velocities of interacting atoms were determined using the Verlet algorithm [13, 25]. The time step was 2 fs. The temperature of the system was maintained constant by correcting particle velocities using the Berendsen thermostat [26, 27]. Initial atom velocities were specified using a random-number generator and had a Maxwell distribution corresponding to a selected temperature. The calculations were accelerated employing a program formulated in the FORTRAN language with the help of the CUDA technique [28].

The medium under consideration was composed of MMA monomer and water molecules and PMMA chains. In the calculations, molecules were considered to be flexible. At the first step of the calculations, the structural parameters of MMA and H_2O (the SPC model) were taken from [15] and [29], respectively. The calculated melting and boiling temperatures of MMA (225 and 383 K) were in good agreement with experimental data.

CALCULATION RESULTS

Initially, the behavior of single PMMA chains was calculated in vacuum. It was revealed that PMMA chains of certain sizes were folded into compact almost spherical particles. In the literature, these formations are commonly referred to as globules [30] the sizes of which are determined from the radii of gyration.

The calculated dependence of the globule formation time on the chain length (degree of polymerization n) is shown in Fig. 1. The calculations were carried out at 300 K in vacuum. It can be seen that the globule formation time increases with the chain length; i.e., globules containing a small number of monomers are formed more rapidly.

Figure 2 illustrates time variations in the conformation of a PMMA chain composed of 320 monomers for trajectory lengths of (a) 10 and (b) 300 ps. It can be seen that, within this time interval, the chain is not folded into a globule. The calculations show that longer PMMA chains are not folded into globules as well.

Under real conditions, spherical structures are formed in a medium composed of water and MMA. PMMA is soluble in MMA, and the medium viscosity varies with variations in the monomer concentration. This leads to variations in the rates of the chain propagation and termination. Therefore, polymerization yields chains with different lengths. These chains can form globules. Therewith, the globule size may depend on water and MMA concentrations.

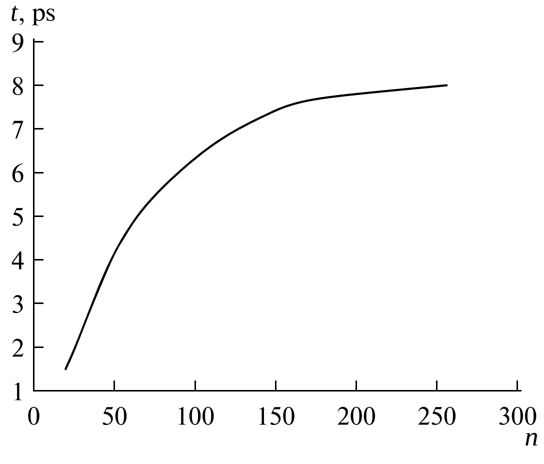

Fig. 1. Dependence of the formation time of globules from single PMMA chains on degree of polymerization n.

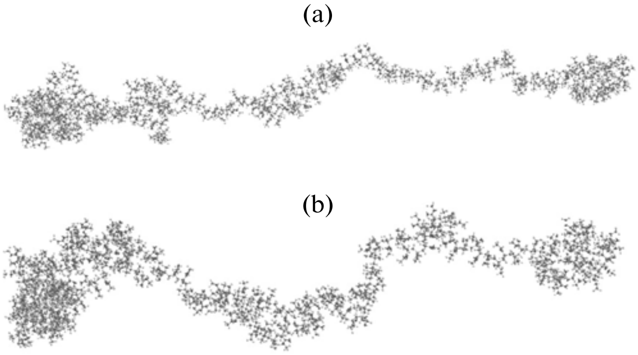

Fig. 2. Time variations in the conformation of a PMMA chain with a length of 320 monomer units at trajectory lengths of (a) 10 and (b) 300 ps.

The calculated dependence of the radius of gyration of a PMMA globule on water concentration in MMA is presented in Fig. 3. At a monomer concentration of 100%, MMA molecules interact with the globule and are present both inside the globule and in its shell; moreover, the calculations show a reduction in the globule radius of gyration. Water molecules are smaller than MMA molecules; therefore, they more readily diffuse inside the globule and, as follows from the calculations, the radius of gyration increases due to variations in the intermolecular interactions and a rise in the distances between monomer molecules. This effect is observed up to water concentrations of ≈30%. In this situation, the globule is enlarged to such an extent that MMA molecules can more readily penetrate into it (Fig. 4). An increase in the local concentration of MMA molecules inside the globule leads to its compression and a reduction in its radius of gyration, with this process occurring up to a water concentration of ≈80%. As water concentration is further increased and MMA concentration is decreased, the number of H_2O molecules inside the globule begins to grow again to vary the effective interaction between MMA and PMMA molecules, with the gyration radius increasing once more.

Variations in the energy of the PMMA–MMA–water system with water concentration in the mixture are illustrated in Fig. 5. An inflection is observed in the dependence at a water concentration of ≈80%. This seems to be associated with a change in the conformation of polymer molecules. Therewith, the gyration radius increases and the terminal groups of the polymer chains become more accessible, which may accelerate the polymerization, because the probability that a monomer molecule will encounter a terminal group of a chain rises.

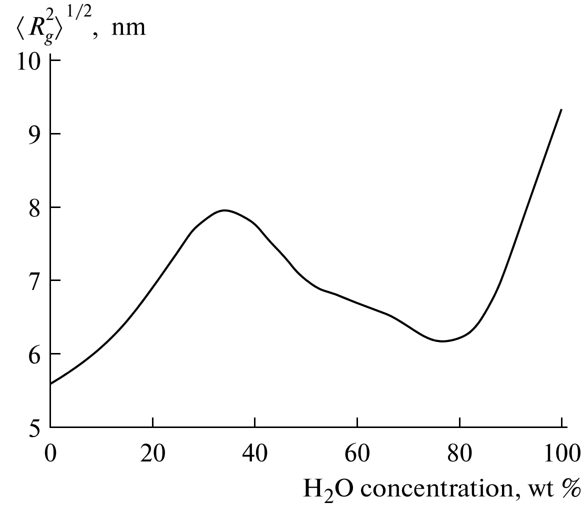

Fig. 3. Dependence of the gyration radius of a PMMA globule on the concentration of water molecules in a solution at 300 K.

The calculations have shown that, when PMMA chains with a degree of polymerization of smaller than 200 occur in a water–MMA mixture, globules composed of entangled polymer chains are formed in the system. Figure 6a depicts a snapshot taken during the assembling of a number of PMMA chains into a globule in a water–MMA medium. Then, due to the entanglement of the PMMA chains present in these globules, the experimentally observed spherical particles are formed from them. In addition to PMMA, these particles contain the water–MMA mixture.

When a larger number of globules (up to 150) occurring in an emulsion medium are involved in the calculation, spherical particles with a diameter of about 100 nm (trajectory length of 600 ps) are formed. In this situation, PMMA chains are entangled with each other, this leading to the coalescence of the primary globules. A spherical particle with a small number of PMMA molecules is exemplified in Fig. 6b.

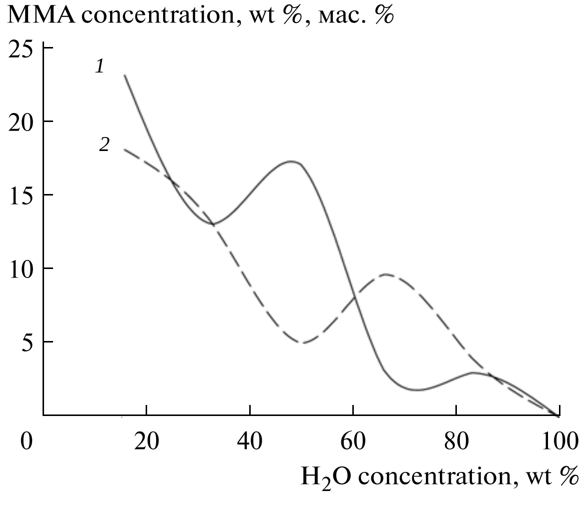

Fig. 4. Dependences of MMA concentrations (*1*) inside a globule and (*2*) in a dispersion medium on the total water concentration in a mixture.

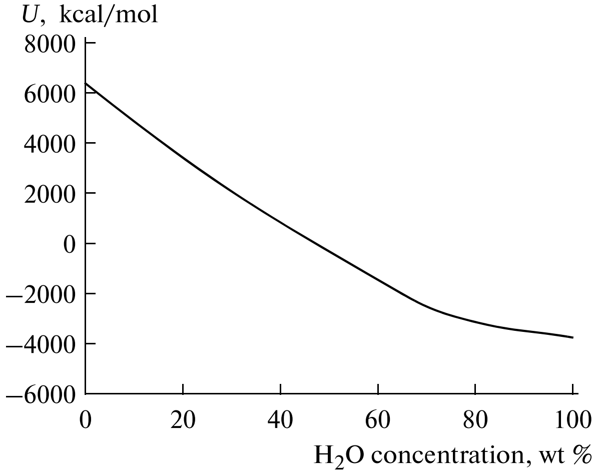

Fig. 5. Variations in the energy of a PMMA–MMA–water system as depending on water concentration in a mixture.

Thus, it may be concluded that spherical particles are formed from globules of smaller sizes owing to their coalescence.

EXPERIMENTAL

Aqueous dispersions of submicron PMMA particles were experimentally prepared by a somewhat modified procedure described in [5, 6]. After the temperature in a reactor was stabilized with the help of a thermostat, temperature fluctuations in the reaction mixture were measured in the regime of dynamic observations (Fig. 7).

In order to establish the optimal conditions for the synthesis of spherical particles, aqueous emulsions with MMA concentrations of 25–50% were studied (here and below, the concentrations are given in weight percent).

The reaction was found to proceed slowly with a low heat release until a monomer concentration of *bc* was reached (time period *bc* in Fig. 7). The polymerization of the majority of MMA then occurred, which was accompanied by a noticeable heating of the reaction mixture for a short time of about 10 min (period *cd* in Fig. 7). Given this, the higher the initial monomer concentration, the longer the slow period of the process and the higher the temperature to which the mixture is heated during its fast period—up to the boiling of the solution.

For mixtures with initial MMA concentration of higher than 40%, the scatter of particle sizes increases with monomer concentration and nonspherical particles can be formed (Fig. 8).

The calculated and experimental data lead us to assume that variations in the PMMA molecule gyration radius at MMA concentrations in water lower than 20% (other parameters being equal) cause variations in the dynamic viscosity of the liquid.

Polymerization is an exothermic reaction. A decrease in the fluidity deteriorates the heat removal from the reaction medium, this promoting a local increase in the temperature and, as a consequence, a reduction in the viscosity. Thus, the system is self-sustaining at the boundary of the sol–gel transition, and this fact promotes a uniform growth of spheres throughout the reactor volume.

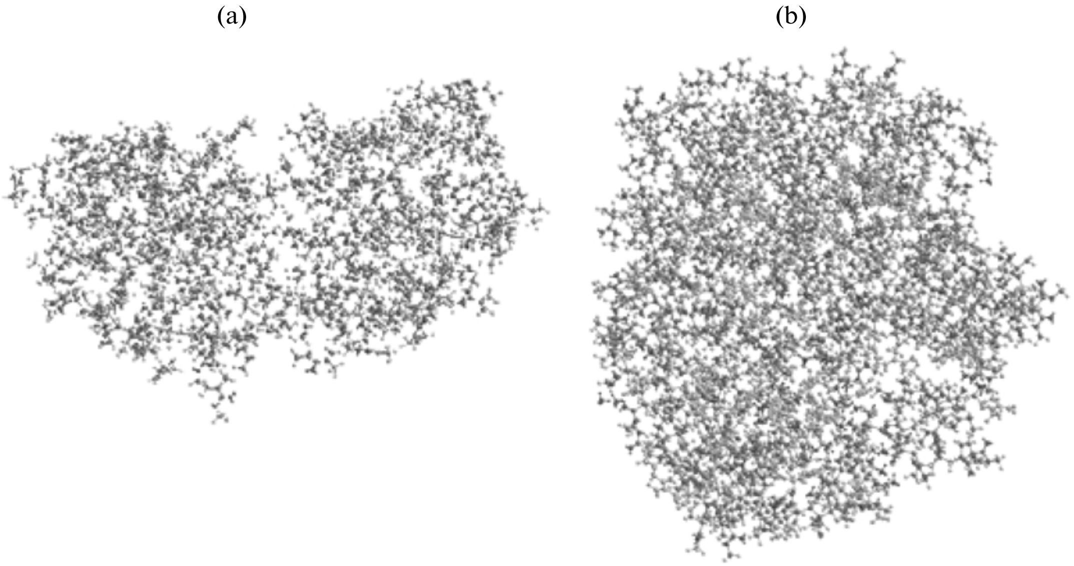

Fig. 6. Panel (a): the onset of the coalescence of PMMA globules in an emulsion medium composed of water and MMA monomer molecules; panel (b): a spherical particle formed from ten globules.

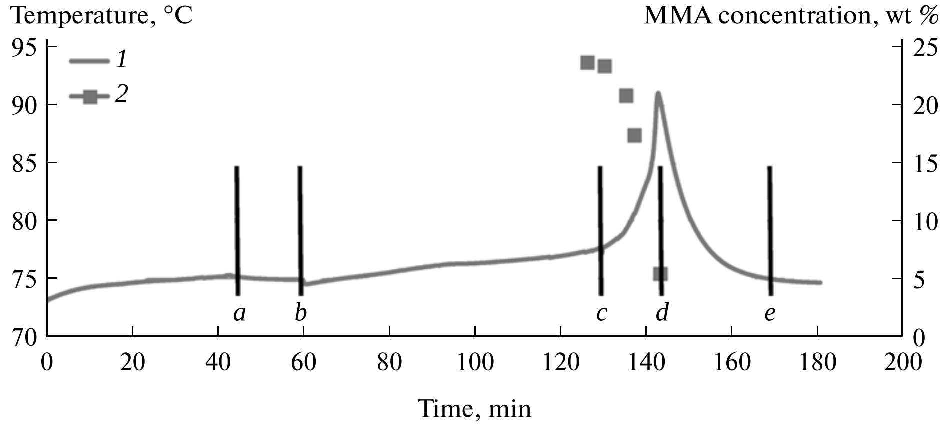

Fig. 7. Time variations of (*1*) temperature and (*2*) MMA concentration in a reaction mixture during polymerization: (*ab*) period of reactor thermostating, (*b*) moment of polymerization initiator introduction, (*bc*) period of reaction with a low heat release, (*cd*) polymerization of the majority of MMA, and (*de*) period of reaction-mixture cooling to the temperature of thermostating.

Moreover, increasing temperature accelerates monomer diffusion, thereby accelerating polymerization via an increase in the probability that a monomer will encounter a terminal group of a chain. The increase in the polymerization rate accelerates the temperature elevation, which, in turn, accelerates the polymerization; therefore, an avalanche-like elevation of the temperature is observed. It is obvious, that the monomer concentration diminishes in the course of polymerization. As the monomer concentration decreases, polymerization decelerates [30]. As a consequence, the temperature of the reaction mixture diminishes.

Thus, when the MMA concentration drops below 20%, the rate of polymerization dramatically increases, this leading to the formation of long chains that form globules, which coalesce to yield spherical particles with equal sizes.

The morphology of PMMA particles was studied using an S5500 electron microscope (Hitachi) with the following basic characteristics: resolution of 0.4 nm, accelerating voltage of 30 kV, and maximal magnification of 2000000×. The accelerating voltage and the measuring current could be varied from 0.5 to 30 kV with a step of 1 kV and from 1 to 10 mA, respectively.

Spheres were found to be porous and shrink under the action of an electron beam (Fig. 9). This was seemingly accompanied by the evaporation of an MMA–water mixture remaining after the coalescence of the globules.

It has been established that, at initial monomer concentrations in a mixture below 25%, spheres are formed with a size scatter of less than 10%. These spheres can already be packed into defectless colloidal crystalline structures (Fig. 10). Therewith, the average sphere diameter can be varied in a range of 100–400 nm.

CONCLUSIONS

Conditions have been determined for producing aqueous dispersions of submicron PMMA particles with uniform sizes. Highly spherical particles are formed at an MMA concentration of ≈23%. MMA and water are present in globules and spherical particles resulting from the synthesis.

Molecular dynamics simulation has shown that spherical particles are formed from several poly(methyl methacrylate) chains rather than single ones. These multichain particles are observed in experiments. The data calculated by the molecular-dynamics method also have indicated the presence of a water–MMA mixture inside the particles. These data show that an MMA concentration in a reaction mixture of 20% is optimal for production of the spher-

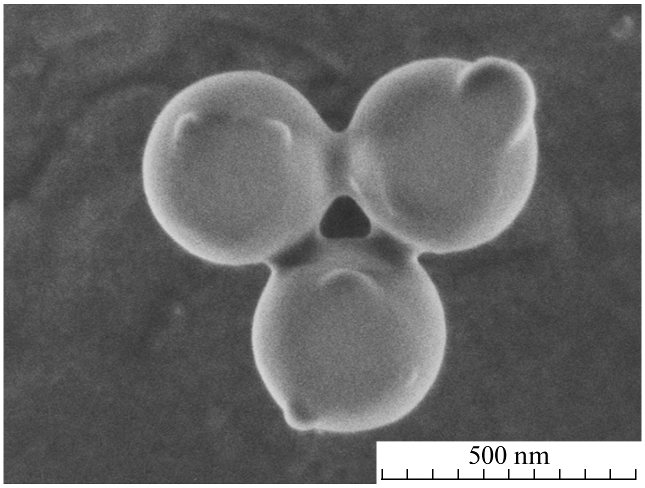

Fig. 8. PMMA particles formed at an MMA concentration of 45%.

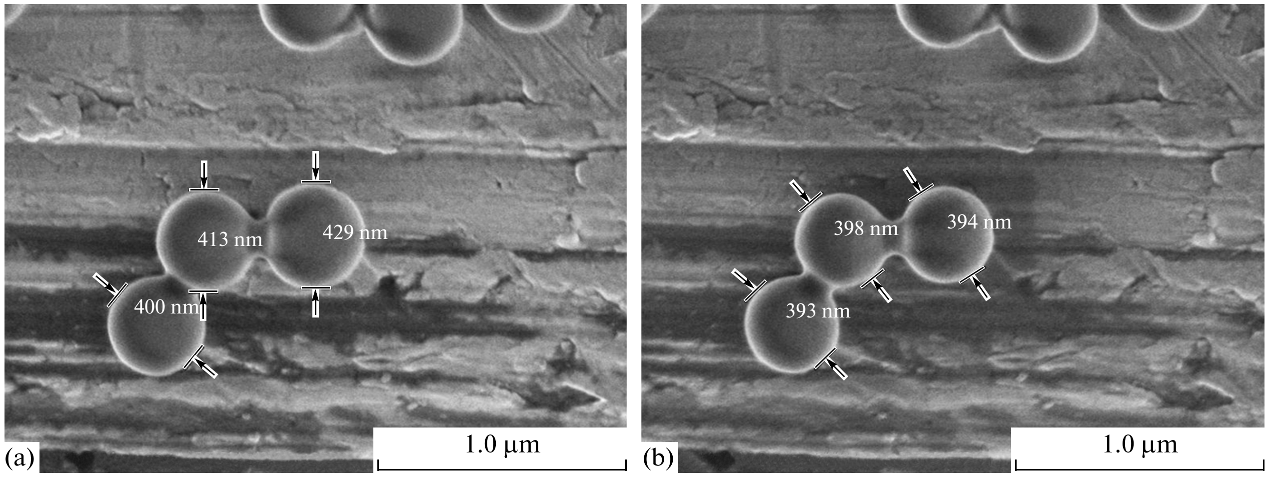

Fig. 9. Spherical particles after (a) short and (b) long exposition to electron microscope beam.

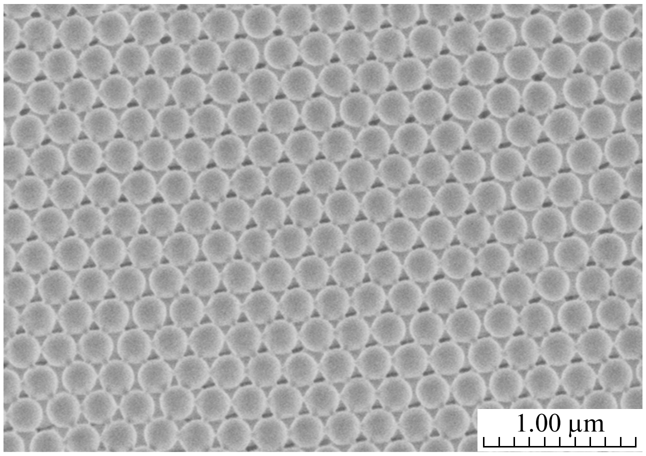

Fig. 10. A layer of spherical PMMA particles at initial MMA concentration of 15%.

ical particles. This result also agrees with the data of real experiments.

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