Features of Self-Assembly of Opal-Like Structures Based on Poly(Methyl Methacrylate) Submicron Dispersions

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Abstract—Features of the formation of periodic 2D and 3D opal-like structures depending on the conditions of deposition have been investigated in this work. The subject of the experiments is aqueous dispersions of poly(methyl methacrylate) submicron particles with a narrow size distribution. The particles are precipitated by sedimentation, centrifugation, and the meniscus method. The samples are studied using electron microscopes. Significant morphological differences in periodic structures obtained by various methods are found.

INTRODUCTION

Over more than half a century ago, the development of electron microscopy made it possible to observe the structure of precious opal [1–3]. Since then, numerous investigations of the synthesis and morphology of such materials have shown that regular 2D and 3D opal-like formations originate from the self-assembly of spherical particles almost uniform in size. Inverted (inverse) opals are obtained in the form of replicas from such polymer structures. The location of pores in inverse opals is a 3D copy of the initial matrix [4].

A wide choice of materials for the synthesis of structural units and techniques of their aggregation makes each method of preparation of opals fairly unique.

The narrow size distribution of spherical particles in the sample enhances the reproducibility of the material structure based on them and helps avoid the formation of defects during their self-assembly into 2D films and 3D objects [3, 5, 6].

In their turn, they can be used as matrices for impregnation with differing solutions and sols capable of forming an optically transparent durable framework upon thermal treatment and the removal of an organic matrix. Inverse and classical opals are photon crystals that exhibit interesting optical properties [7].

The aims of the present work are investigating the structure of the synthesized poly(methyl methacrylate) (PMMA) spheres and investigating features of self-assembly of periodic structures based on aqueous dispersions of PMMA particles.

SYNTHESIS OF PMMA MICROSPHERES

A necessary condition for the formation of dispersions of PMMA submicron spheres with a narrow size distribution is a short phase of intense multiple nucleation followed by a slow controlled growth of particles with keeping their number constant. The process of free-radical chain polymerization of methyl methacrylate (MMA) can be conventionally divided into three steps: initiator activation, a reaction between a monomer and an initiator radical and molecule growth, and polymer chain termination [8]. Upon heating, the initiator decomposes with the formation of free radicals, which are initiators of a polymerization reaction [8, 9].

Upon conducting experiments on obtaining aqueous dispersions of PMMA submicron particles [5, 10–12], 2,2'-azobis(2-methyl propionamidine), which features a lowered probability of side disproportionation and chain transfer reactions, was applied as an initiator.

Upon stabilization of the reactor wall temperature at 75°C, measurements of variations in the reaction mixture temperature were made in the mode of dynamic observation (Fig. 1). At the same time, the IR spectrum of the mixture was recorded with the help of an FT-801 IR Fourier spectrometer with a fiber probe
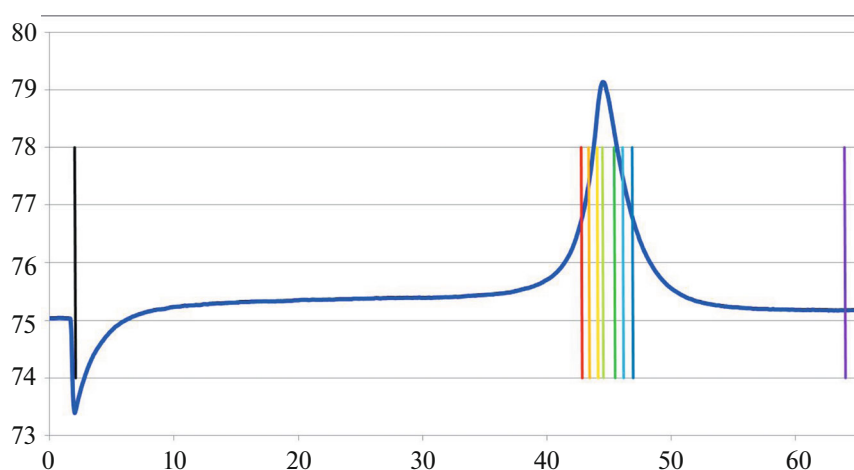
Fig. 1. (Color online) Changes in the reaction mixture temperature during the MMA polymerization. Here, the *x* axis is the time from the beginning of the experiment (min) and the *y* axis is the reaction mixture temperature (°C); a sharp decrease in the reaction mixture temperature before the beginning of the reaction is caused by the introduction of the initiator solution. Colored vertical lines indicate the moments of recording spectra of the mixture (see Fig. 2).
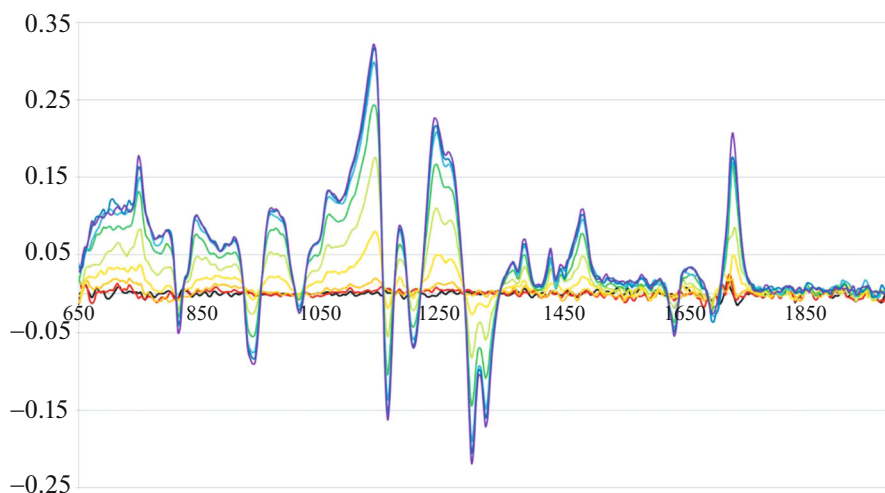
Fig. 2. (Color online) Changes in the observed spectrum of the reaction mixture during the polymerization. The color of the spectrum corresponds to the color of the marking line of the spectra recording moment in Fig. 1. *x* axis is the wavenumber (cm^{-1}) and *y* axis is the relative change of the spectrum from the initial one.

with a frustrated total internal reflection (FTIR) sensitive element (the measurement range was 500 to 2600 cm^{-1} and the resolution was 8 cm^{-1}) (Fig. 2).

The polymerization reaction proceeds with a prolonged slow heating of the reaction mixture at the initial steps of the particle growth and a sharp increase in temperature at deep reaction steps, because a hard gel effect is typical of MMA polymerization [8, 11, 12].

Changing the MMA concentration, the amount of the introduced initiator, the rate of reaction mixture stirring, and temperature mode in the reactor allows controlling the sizes of the obtained particles.

As a result, dispersions of PMMA spherical particles with a diameter from 100 to 500 nm with a rather

a narrow size distribution were prepared without adding emulsifier, stabilizers, etc.

MORPHOLOGY OF STRUCTURES FROM PMMA SPHERES

For the formation of PMMA matrices, three techniques were employed in the present work: natural sedimentation [3], centrifugation [3], and deposition in a meniscus upon the evaporation of a dispersion medium [6, 13].

To obtain a replica, the process of impregnation of the PMMA matrix should be carried out in such a way so as not to provoke its cracking due to disjoining pres-
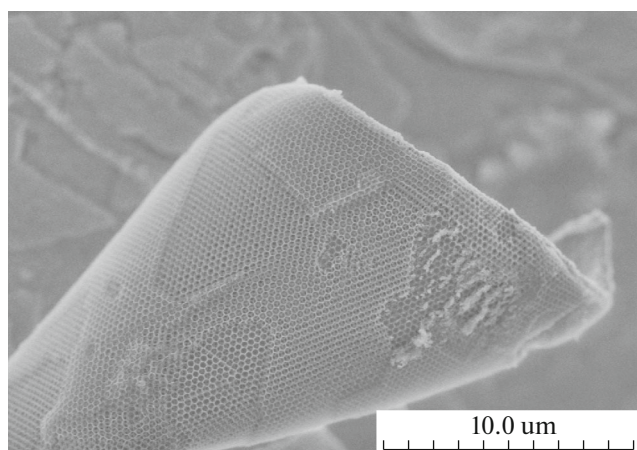
Fig. 3. Replica exfoliation caused by nonuniformity of crust drying.

Fig. 4. (Color online) Shrinkage of PMMA particles under the action of an electron beam.

sure in the intersphere space. For this, the rate of penetration of liquid into the template can be lowered by changing the impregnation viscosity, and the conditions of drying and annealing of the obtained materials can be chosen carefully.

The methods of impregnation are described in [5, 14]. Herein, silica alcosols and aqueous−alcoholic solutions of the products of foamed silicate leaching of an aluminosilicate system were used.

Crust formation during impregnation can be accompanied by the appearance of mechanical stresses and lead to the formation of an exfoliated 2D replica (Fig. 3).

The resulting objects were investigated on S5500 and HT7700 electron microscopes (Hitachi).

It was found that, under the action of an electron beam, the spheres contract, with the rate of contraction depending on the current density. The current density, in its turn, depends on the scanning area. Therefore, increasing the magnification for the examination of a certain sphere, we observe its quick (of several seconds) contraction. In Fig. 4, the initial particle outline is shown in green; the particle outline after the local action is indicated in red. The decrease in the diameter can reach 25%.

A supposition was made that the spheres contain nanopores filled with a gas or liquid. As a result of local heating of a certain particle with an electron probe, the contents of nanopores is liberated, they collapse, and the sphere contracts. The particles of a pure polymer lose their shape when melted, spreading over the substrate.

The presence of bound water in polymer spheres is corroborated by spectral data shown in Fig. 5 (Vertex-80v BRUKER instrument). Some peaks in the range of 3400−3700 cm^{-1} disappear after deep melting. At the same time, the main spectrum remains
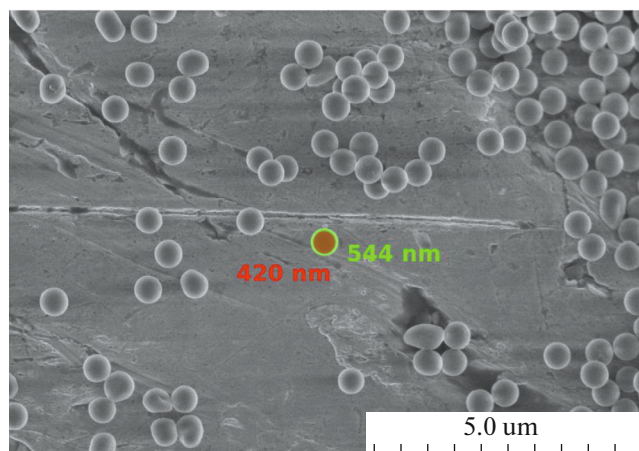
unchanged, which is evidence that decomposition of PMMA did not take place.

The application of a centrifuge for deposition considerably shortened the time it takes to prepare the opal-like structure; however, the domain sizes became significantly lower than upon natural gravity sedimentation (tens of micrometers against units of millimeters). Upon centrifugation, particles that cannot go into a crystal lattice due to their large sizes are squeezed out into the interdomain wall (Fig. 6).

Upon natural sedimentation, large domains visible to the naked eye result (Fig. 7a).

Note that, when using dispersions with an elevated residual MMA content, the shrinkage of particles while mutual bridges are kept takes place (Fig. 7b). Therefore, the relative value of the interparticle space volume increases.

Upon the formation of opal-like structures in a meniscus, a single crystal with vacancies and linear defects forms at the substrate (Fig. 8). The volume of such an ordered matrix reaches several tens of cubic millimeters. One should make a special emphasis of the fact that self-healing of the crystal lattice is interrupted only by a 2D defect (a domain wall).

The investigation of dispersions strongly dissolved with water on a transmission electron microscope revealed that the region of mutual contact of spheres with one another has a higher density than the average density across the volume (Fig. 9). The same is true for the places where the spheres attach to the substrate. Dark zones in the spots of contact of spheres with one another and dark spots at the places of attachment to the substrate imply higher energy losses of transmitted electrons, which is usually associated with an elevated matter density. One may thus suppose that the mechanical strength in the spots of contact is raised; therefore, sticking together has an irreversible character.
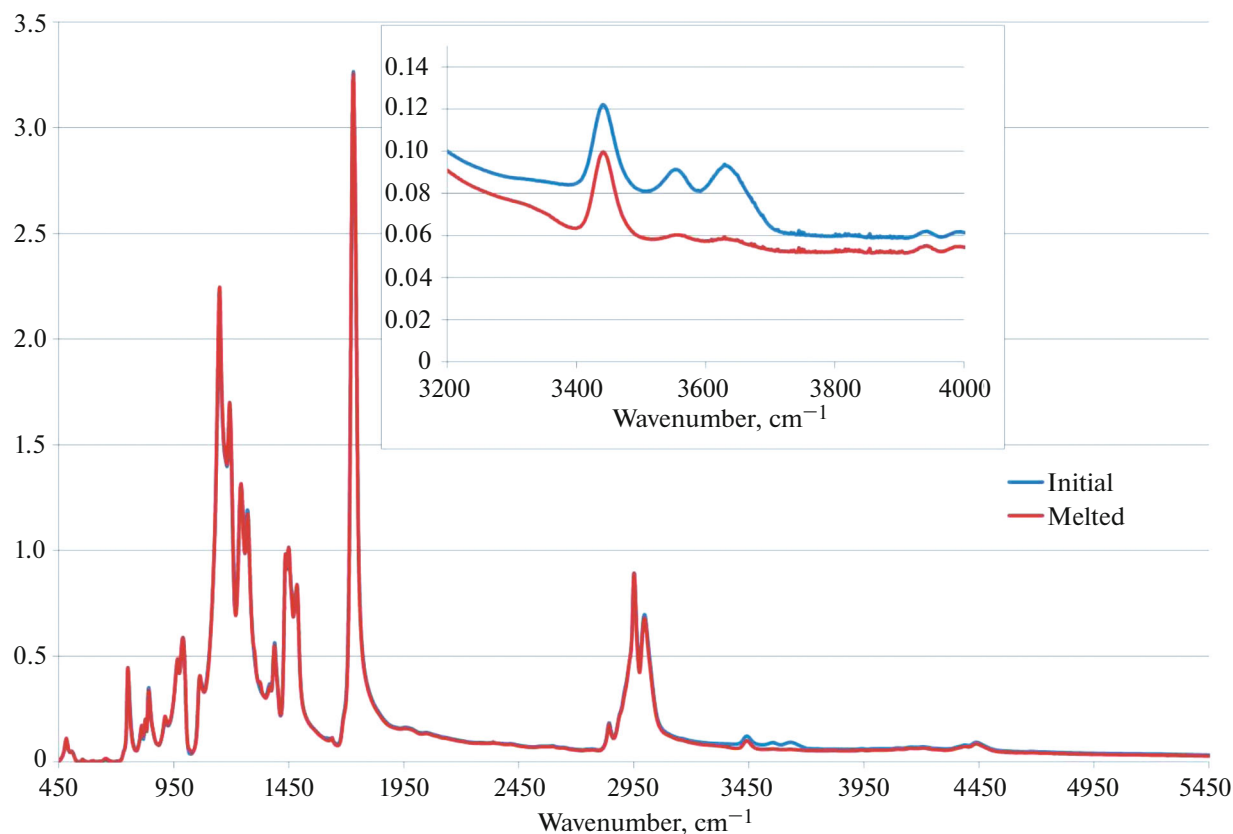
Fig. 5. (Color online) IR absorption spectrum of the initial dry and melted PMMA samples.

CALCULATING PMMA GLOBULE STRUCTURE

Using the molecular dynamics technique, calculations of a conformation of the PMMA chains formed in a media comprising water and a MMA monomer
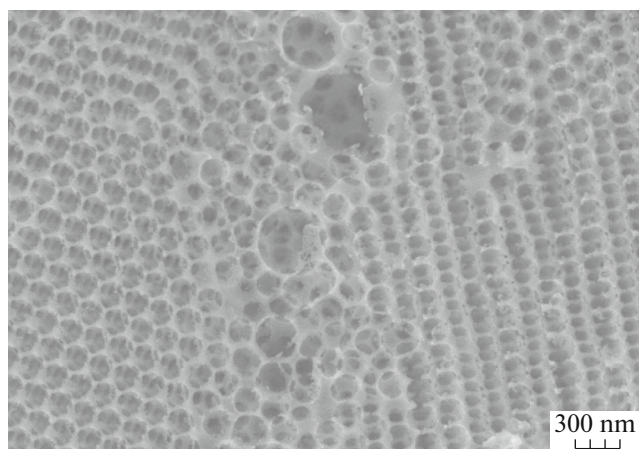

Fig. 6. Interdomain boundary into which incommensurate particles were squeezed out.

were made. This technique is described in detail in a number of works [15]. The motion equations of a system of interacting particles are set up and the paths of particle motion are obtained upon integration.

Since the behavior of flexible molecules was investigated, the interaction potential is represented in the form

$$U = U_s + U_b + U_t + U_{vdW} + U_e,$$

where U_s is the potential energy of valence bonds, U_b is the potential energy of valence angles, U_t is the potential energy of torsion angles, U_{vdW} is the potential energy of van der Waals interactions, and U_e is the potential energy of Coulomb forces.

The vales of coefficients in the U_s, U_b, U_t, and U_e potentials for MMA are given in publications [10, 16] and were used in calculations. To describe the intermolecular interaction, the method of atom−atomic potentials was employed [17]. The coordinates and velocity of atoms during interactions were determined using the Verlet algorithm [18]. The time step was 2 fs. The system temperature was kept constant through correcting the particle velocity.
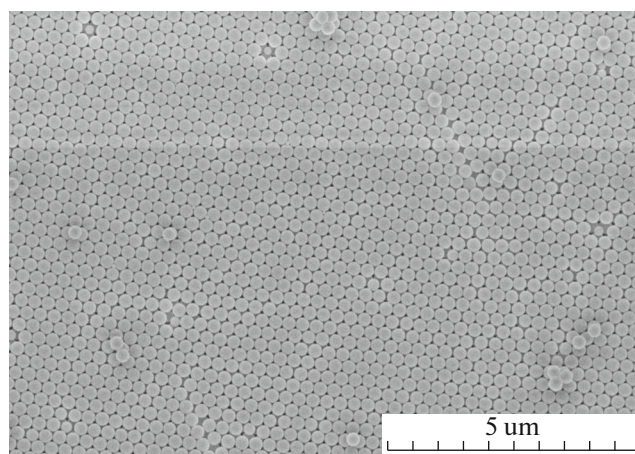
Spherical particles composed of PMMA globules result in the reactor upon vigorous stirring. Depending

(a) 1 um

5 um

Fig. 8. Single crystal with defects obtained by meniscus method.

(b) 1 cm
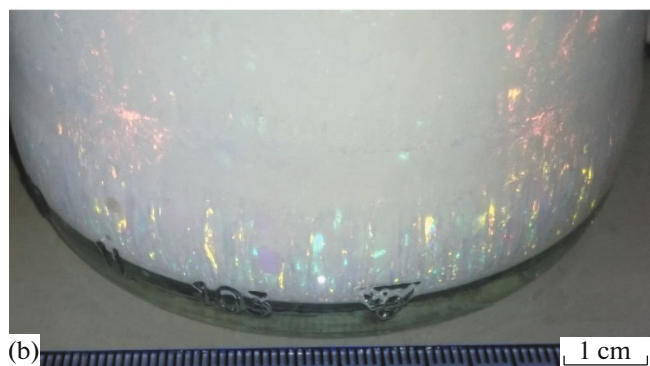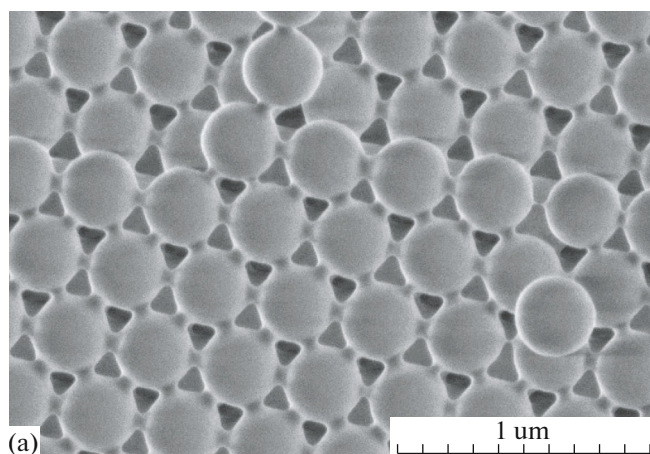
Fig. 7. (Color online) (a) Domains obtained upon natural sedimentation. (b) Domain microstructure with bridges between particles.

on the stirring rate, the diameter of globules and microparticles formed from them can vary. Therefore, the behavior of a mixture of water, MMA, and PMMA in the reactor was simulated; with allowance for a hydrodynamic flow, it was also determined under the following assumptions: the liquid was placed between two planes, one of which was immovable and another one was moving at a certain speed (for simulation of a

stirrer action in the reactor). Initially, concentrations of the components and the degree of PMMA polymerization were specified. A globule containing water and MMA forms as a result (Fig. 10). It is seen that a portion of water and MMA molecules occur within the globule, and, around the globule, the considered medium is composed of MMA monomer molecules and water.

Simulation of interaction between two globules (Fig. 11) showed that, in the spot of contact, interpenetration of PMMA chains surrounded by water and MMA molecules takes place. As was noted in work [10], spherical microparticles comprise globules with interwoven PMMA chains. Upon interaction between two microparticles, the analogous (as for the case of two globules) interpenetration of PMMA chains surrounded by water and MMA molecules occurs. This agrees with the observed bonding depicted in Fig. 9.

The microparticles lose their spherical shape arranging on the substrate, which is confirmed by cal-


(a) 200 nm (b) 200 nm
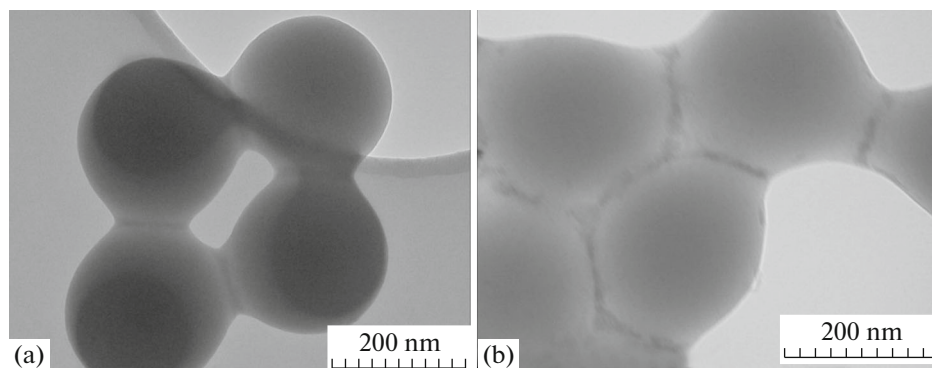
Fig. 9. Microphotograph of groups of PMMA spheres in a transmission electron microscope. The spheres are supported in the electrom beam with the help of a carbon film.
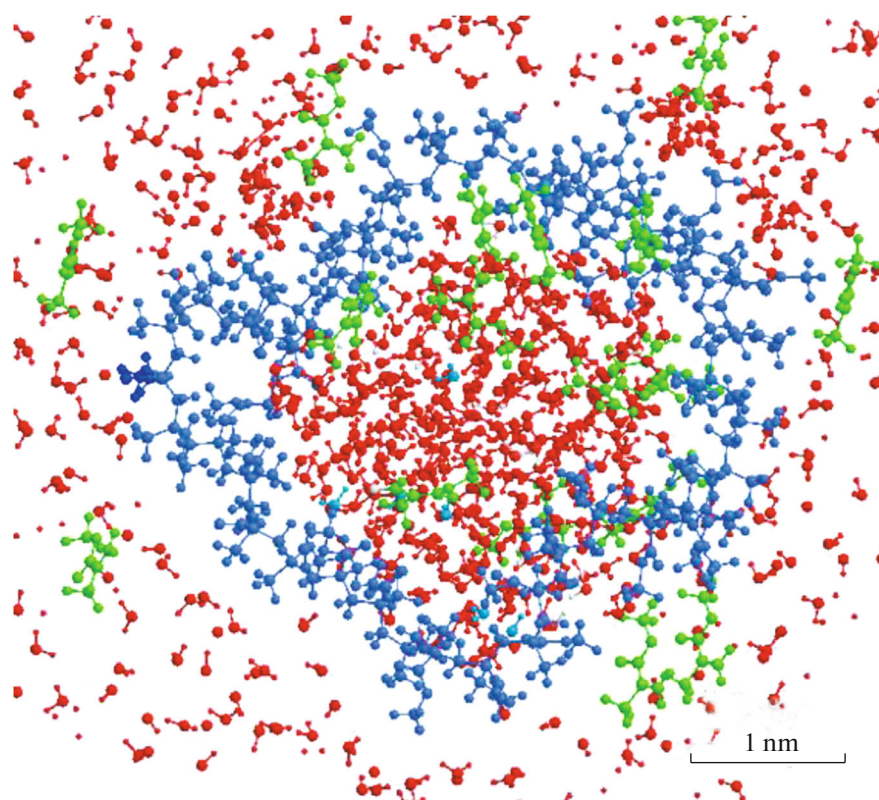
Fig. 10. (Color online) Section of a part of a PMMA globule (blue) with water (red) and MMA molecules (green). For simplicity, only 10% of molecules are shown outside the globule.

culations. The PMMA chains approach the substrate, changing the spherical shape of a particle. As it does, an interlayer from water and MMA forms between the substrate and the particle.

Thereby, the calculations confirm that water molecules are present in the PMMA globule structure and the density of globules is elevated in the spots of contact with a substrate and with one another.
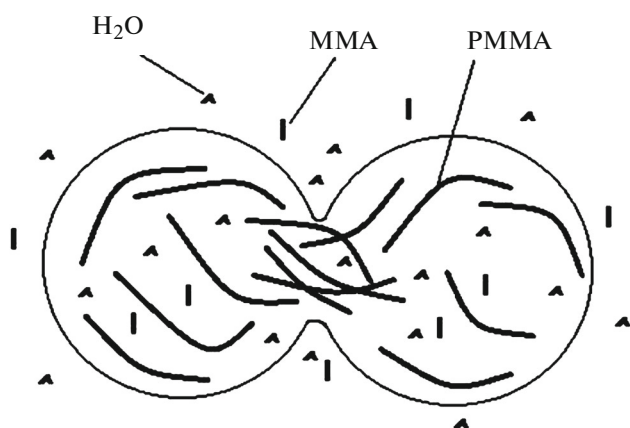
Fig. 11. Calculation of the location of molecules upon the contact of two PMMA spheres.

CONCLUSIONS

The process of formation of PMMA globules begins in the mixture of water and a monomer in the presence of an initiator. On achieving a certain length, polymer chains start to roll up and group into globules.

The sizes of globules depend on the length and number of polymer chains, and the number of water and MMA molecules enclosed by them.

The globules of the same size unite into spherical particles similar in dimensions.

In capillaries that stemmed from globules sticking together, there are water and a monomer, which are removed upon drying, yielding a shrinkage of up to 5%.

The water contained in globules can be removed only by annealing with an up to 25% decrease in the sphere size.

In the spots of contact between spheres, areas with an elevated density are formed.

The presence of unconverted MMA in dispersions can promote the formation of bridges between PMMA particles in a direct opal due to a decrease in the volume of the spheres upon drying. An increase in the intersphere space volume provides more durable inverse opals.

Mechanical action affects the self-assembly process: small domain sizes upon centrifugation are caused by vibration. The latter, in its turn, also squeezes defect pores from microdomains out.

Upon natural sedimentation, the mechanical action on a precipitating suspension can also result in the interruption of domain growth and the beginning of their reconstruction from scratch.

Upon growing in a meniscus on a flat substrate, even the presence of point and linear defects does not result in a polydomain structure of a self-organizing crystal.

ACKNOWLEDGMENTS

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