A simple geometrical model for emulsifier free polymer colloid formation

Chiara Dionigi,* Petr Nozar,* Davide Di Domenico,* and Gianluca Calestani b

* Istituto per lo Studio dei Materiali Nanostrutturati—Bologna Div, Consiglio Nazionale delle Ricerche, Via P. Gobetti, 101, I-40129 Bologna, Italy
b Dipartimento di Chimica Generale ed Inorganica, Università di Parma, viale delle Scienze, I-43100 Parma, Italy

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Abstract

In this paper we propose a simple model for the formation of monodisperse polymer colloids, which provides a convenient set of synthetic parameters for given bead diameters. We provide experimental data in support of this model.

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1. Introduction

Polystyrene beads represent one of the most used polymer colloids (latex) and several studies have been performed to control the bead size and monodispersity since the thirties of the previous century. The water–styrene emulsion has been extensively studied over the past 30 years for various applications in material science, chemistry, and biology [1–8]. New methodologies for synthesizing polystyrene beads are still relevant because they provide accessible chemical methods to obtain micrometer-sized particles with a given shape and size and a monodispersity even less than 2%. Indeed, the spherical shape allows the self-assembly of such beads into crystalline arrays, with lattice periodicities comparable to their diameters [1,9,10]. Such arrays also function as removable templates for the fabrication of three-dimensionally ordered porous materials and find fascinating applications in the field of photonic band gap materials [11] as found in the abundant literature in this area. Surface bead modification (e.g., dye doping) or lattice infiltration with active dopant have been used [12] to control the photonic band gap by combining the bead lattice periodicity with dye properties (e.g., wavelength-sensitive refractive index).

The early procedures adopted for the reaction involved the addition of a surfactant that helps the “compartmentalization” of styrene in water. However, since the surfactants could contaminate the surface of the bead, a soapless reaction was proposed in 1965.

Several different mechanisms have been proposed for such emulsion polymerization in water without the use of a surface-active agent. These studies [2–6,13–15] are concerned primarily with particle formation and growth. Three basic mechanisms have been suggested: (i) homogeneous nucleation, (ii) homogeneous–coagulative mechanisms, and (iii) in situ micellization. These proposed mechanisms for bead synthesis essentially consider three reaction stages [3–6,13–15]. The first step concerns charged oligomer formation from initiator decomposition and subsequent “precursor nucleus” formation depending on the degree of polymerization. The colloidal suspension of such precursor nuclei is unstable and the nuclei coagulate into a stable suspension of “mature nuclei.” The second stage of the reaction involves growth by polymerization of monomer on each monomer-swelled mature nucleus [2,13–15]. The third stage is the termination of the reaction associated with the depletion of monomer. The studies reported in the literature have mainly concerned nucleus formation and growth. The observed dependency of the nucleus size, and hence the nucleus concentration, on synthesis parameters is described in the literature [2–6], but there are no simple models for the prediction and control of bead size and concentration in latex suspension. In this communication we propose a general model, independent of any polymerization mechanism, to predict the bead diameter and to provide experimental parameters to control the concentration of latex particles. This model is supported by experimental data.
2. Materials and methods

2.1. Preparation of latex

The syntheses of charged latex were performed by emulsifier-free polymerization of styrene in water using potassium persulfate (99% Aldrich, negatively charged beads) or 2,2'-azobisisobutyronitrile (97% Aldrich, positively charged beads) as initiators. A fresh batch of styrene was prepared by removing the polymerization inhibitor (tert-butylcatechol) with an inhibitor removal column under nitrogen atmosphere. In a 500-ml three-neck round-bottom flask, 200 ml of freshly boiled deionized water was mixed with styrene (Aldrich, 99%) under mechanical stirring. The reagent mixture was heated under reflux. The reaction started at 75 °C, when 0.9 × 10⁻³ mol of the initiator was added. The stirring rate was fixed at 500 rpm. The temperature was kept constant during the entire synthesis. The reaction was stopped after 24 h.

For beads with a diameter (D) smaller than 220 nm, a small amount (5-10 vol%) of ethanol was added to the water.

The reaction procedure was performed both under natural light and in the dark with the same results.

A two-step process was used for the preparation of beads with a diameter larger than 450 nm. In the first step, beads with a smaller diameter (usually 340 nm) were prepared according to the procedure described above. In the second step the monomer was added continuously to the first-step dispersion at a low rate (0.03 ml/min). All other parameters were kept constant and equal to the parameters of step one.

2.2. Aggregation of latex

For latex aggregation the centrifugation method of the bead suspension was used. A sample of 10 ml of the latex dispersion was poured into a polypropylene test tube and centrifuged at 350–1050g for at least 10 h. The sediment was dried at 50–70 °C for 4 to 12 h to eliminate the residual swelling monomer.

2.3. Yield determination

The yield of the bead formation reaction was gravimetrically determined. A measured volume of latex dispersion was centrifuged following the method described above. The residue was dried at 50–70 °C for 4 to 12 h and weighed. The yield was calculated by considering the ratio between the obtained solid residue and the expected one. The expected residue was calculated by considering a complete transformation of styrene into polystyrene and neglecting the weight change due to chain-ending groups, mainly coming from the initiator.

2.4. Characterization

The diameter of the beads was determined optically by measuring the absolute reflectivity of the bead aggregate.

The home-built optical system for absolute reflectivity measurement is composed of seven basic units: a 300-W xenon lamp; a computer-controlled monochromator; a beam splitter; a 2θ–2θ stage with sample holder; two light detectors (photomultipliers); and a computer controller. The light beam is produced by the xenon lamp and is concentrated by the lens into the input slit of the monochromator. Monochromatic light from the output slit of the monochromator is divided into the measurement beam and the reference beam (ratio ≈ 95% to 5%, respectively) by the beam splitter. Then the measurement beam is focused by the optical path onto the surface of the sample (diameter of the spot ≈ 0.1 mm). The sample is mounted on the sample holder, which can be micrometrically adjusted linearly in three perpendicular directions and rotationally around three mutually perpendicular axes. The sample holder is fixed on the manually controlled 2θ–2θ stage. The reflected measurement beam and the reference beam are collected by the measurement beam photomultiplier and the reference beam photomultiplier, respectively. The calibration of the reference signal is carried out by spectrum measurement with the sample substituted by the measurement beam photomultiplier before and after every set of spectra measurements.

The shape and diameter of the beads and the quality of the surface of aggregated samples were determined by atomic force microscopy (AFM) and the same samples were then checked by scanning electron microscopy (SEM).

AFM measurements were performed using a Topometrix TMX 2010 apparatus. The apparatus is calibrated by the measurement of the silicon microgrid with the grid step 2–24 μm. Additional calibration was performed using commercial latex (Aldrich) with diameters in the range of 100–800 nm.

SEM analyses of the bead crystals were performed using a Philips XL30 electron microscope operating at 30 kV accelerating voltage. The surface of the samples was metalized by sputtering a layer of gold 1–2 nm thick.

3. Results and discussion

3.1. Determination of the bead diameter

The bead diameter was determined from the blue shift of the reflection maxima in the optical spectra measured on self-assembled samples of beads [12]. Combining the Bragg and Snell law with the condition

\[ \frac{dn}{d\lambda} = 0, \tag{1} \]

which is valid for the ordered bare bead samples (n is the refractive index of the polystyrene used for the beads), a formula for the evaluation of the diameter D of bare beads from
Fig. 1. Comparison of bead diameters obtained by optical and AFM measurements (dotted line corresponds to the relation $D_{\text{optical}} = D_{\text{AFM}}$).

Fig. 2. AFM image of self-assembled polystyrene beads.

optical measurements was obtained,

$$D = \frac{1}{2} \left[ \frac{\lambda_0^{\text{max}} - \lambda_\gamma^{\text{max}}}{[\cos(2\gamma B) - \cos(2\gamma)]} \right]^{1/2},$$

(2)

where $\lambda_0^{\text{max}}$ and $\lambda_\gamma^{\text{max}}$ are wavelengths corresponding to positions of the reflection maximum in the reflection spectrum [12] for incident beam angles $\gamma_0$ and $\gamma$ (measured with respect to the normal to the surface of the sample), respectively.

The diameter of the beads was also estimated from different sets of AFM measurements performed on self-assembled samples by centrifugation. Comparisons of the results of the optical measurements evaluated using relation (2) and the results of measurements of bead diameters by AFM are reported in Fig. 1, where the excellent agreement of the results of these two experimental methods can be seen. The absolute deviation of the bead dimension was determined by measuring the minimum and the maximum bead diameters in each $14 \times 14 \, \mu\text{m}$ AFM sample image (Fig. 2). The resulting absolute deviation of the diameter of self-assembled beads is <5%.

Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Styrene/water [vol%]</th>
<th>Ethanol/water [vol%]</th>
<th>Bead mean diameter [nm]</th>
<th>Absolute deviation [%]$^a$</th>
</tr>
</thead>
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<tr>
<td>L1</td>
<td>0.25</td>
<td></td>
<td>150</td>
<td>7</td>
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<td>L2</td>
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<td></td>
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<td>5</td>
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<td></td>
<td>245</td>
<td>4</td>
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<tr>
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<td>4</td>
</tr>
<tr>
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<td></td>
<td>265</td>
<td>4</td>
</tr>
<tr>
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<td></td>
<td>296</td>
<td>3</td>
</tr>
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<td></td>
<td>402</td>
<td>5</td>
</tr>
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<td>537</td>
<td>3</td>
</tr>
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<td>5.00$^c$</td>
<td></td>
<td>489</td>
<td>2</td>
</tr>
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<td></td>
<td>284</td>
<td>5</td>
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<tr>
<td>Lx2$^d$</td>
<td>0.50</td>
<td></td>
<td>220</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ Absolute deviation of diameter, determined by AFM measurement performed on the surface of the aggregated samples.

$^b$ Beads obtained by two-step seed method.

$^c$ Total styrene/water ratio after two steps: 2.5% + 2.5%.

$^d$ Positively charged beads.

Fig. 3. Latex diameters resulting from different preparation methods: $\square$ positively charged beads; $\blacktriangle$ negatively charged beads; $\times$ negatively charged beads prepared by the two-step seed method; $\bullet$ beads prepared with the addition of 5 vol% of ethanol; $\blacklozenge$ beads prepared with the addition of 10 vol% of ethanol. Dotted line is the fit according to Eq. (6).

3.2. Geometrical approach to latex formation

Results of the latex syntheses are given in Table 1. In Fig. 3 we have plotted the dependence of the latex bead diameter on the volume ratio of the monomer (styrene) in water, keeping all the other parameters constant. The same synthesis procedure was applied for both negatively and positively charged beads. Bead diameters were determined as mentioned above. The plot for the synthesis of negatively charged beads is shown by triangles, while squares represent the corresponding plot for positively charged beads. The two plots are nearly the same so that, within experimental error, bead formation does not seem to depend on the sign of the initiator charge. Instead, it depends on other reaction
conditions such as the concentration of the initiator and the styrene/water ratio.

We have found a simple model that quantitatively predicts the diameter size as long as there is no interaction among the beads. The model is based on the following assumptions [3–6,13–16]: “critical-chain oligomers” resulting from the early stages of the polymerization, control the precursor nucleus formation; the number of mature nuclei does not change significantly and depends on the precursor nuclei; the diameter of the mature nuclei increases until the end of the polymerization reaction.

Usually the average polystyrene molecular mass is on the order of $10^5$–$6$. The contribution of the initiator to the weight of the beads in this case can be considered to be negligible. During the radical polymerization, the formed polystyrene bead corresponds to an equivalent mass of reacted styrene. Varying the amount of total styrene the final bead diameter ($D$) also varies.

The concentration of styrene available to the radical initiator may be taken as nearly equal to that obtained from the solubility of styrene in water. The concentration of stable polystyrene nucleation centers and, therefore, the number of the beads, $N_{sp}$, is kept constant for the same temperature and initiator concentration. The final polystyrene bead diameter ($D$) depends on the volume ratio of the initial styrene. In particular, from the general formula for sphere volume, $V_{sp} = (4/3)\pi r^3$, the bead diameter results:

$$D = 2\left[V_{sp}/((4/3)\pi)\right]^{1/3}.$$  

(3)

For monodisperse latex dispersion, bead volume can also be calculated from polystyrene mass density,

$$V_{sp} = M/(N_{sp}d_{sp}),$$

(4)

where $M$ is the total synthesized polystyrene mass, $N_{sp}$ is the bead number, and $d_{sp}$ is the polystyrene mass density ($\approx 1.05 \times 10^3$ kg/m$^3$).

The total polystyrene mass is correlated with the amount of starting styrene and to the polymerization yield ($Y$) according to

$$M = C_{st}V d_{st}Y,$$

(5)

where $C_{st}$ is the styrene/water volume ratio, $V$ is the water volume, and $d_{st}$ is the styrene density ($\approx 0.909 \times 10^3$ kg/m$^3$).

Then, from relations (3)–(5), it results that

$$D = A(C_{st})^{1/3},$$

(6)

where $A = 2\{(V Y d_{st})/(N_{sp}(4/3)\pi d_{sp})\}^{1/3}$.

In Fig. 3, the experimental data fitting according to (6) is shown. From the fitting it is possible to extract the bead number that, for the reported set of syntheses, results in $N_{sp} \approx 7 \times 10^{14}$ in one liter of dispersion, if an experimental mean yield of the bead formation reaction $Y = 80\%$ is considered. The obtained $N_{sp}$ is in agreement with the data reported in the literature [1–6,15]. Hence, the reported geometrical model is supported by the experimental result reported in Fig. 3. One may, therefore, obtain a controlled bead concentration in the “two-step process” when the second step is performed slowly so that there is only bead-swelling and growth without new nucleation centers being introduced.

The bead diameter may be changed both by terminating the reaction before the styrene has been fully consumed and by increasing the number of nucleation centers, keeping the amount of consumed styrene constant. The latter condition can be achieved by increasing the solubility of the monomer in water by adding a solute (we used ethanol) that affects the solubility of styrene. However, for a given amount of the monomer (without changing the other conditions of synthesis) and for a modified solubility, it must be taken into account that the initiator concentration must exceed the solubility of styrene. From the expressions (6), the consequent increased number of mature nuclei, $N_{sp}$, decreases the bead diameter. Circles in Fig. 3 represent the results of such experiments.

4. Summary

A simple geometrical model that does not depend on the polymerization mechanism can predict bead size and the concentration of monodisperse latex particles in suspension.

The model accurately reproduces the experimental results and agrees with the data fitting reported in the literature [2]. This general method could, in principle, be extended to other emulsion polymerization methods for the synthesis of colloidal bead suspension.

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