Measuring the swelling behavior of polymer microspheres with different cross-linking densities and the medium-dependent color changes of the resulting latex crystal films

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Abstract

We measured the size changes of cross-linked polymer microspheres of narrow size distribution with different cross-linking densities by the in situ swelling method. The swelling behavior of these cross-linked polymer microspheres revealed that their maximal swelling degree linearly decreased as a function of the cross-linker content from 6.65 at 1.36 mol% to 2.43 at 3.25 mol%. By means of UV–vis spectra, we observed the spectral changes of the latex crystal films composed of these cross-linked polymer microspheres when we filled the interstices of the latex crystal films with different fluid media. Some succeeding peak shifts were observed, which may have resulted from the movement or the swelling of the polymer microspheres in the latex crystals.

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1. Introduction

As building blocks, polymer microspheres of narrow size distribution are promising starter materials for fabricating latex crystals as the scaffolds of functional materials such as multiporous materials and photon band gap (PBG) materials. Among other important and useful reasons, controlling and tuning the optical properties of these latex crystals have been attracting considerable attention for their application in optical and optoelectronic devices such as photon crystals and filters [1–8]. Recently, colloids and functional polymer latices of narrow size distribution have been of interest in optics, magnetism, electronics, colloid chemistry, biochemistry, and medicine [9–17]. For example, cross-linked polymer microspheres, allowing changes in diameter induced by changes in temperature and solvent, are of growing importance in a number of applications for rheological control [18,19], for sensitive gels [20–23], and for enhancing the performance of other polymer materials and constructing some microstructures [24,25]. The swelling degree or cross-linking degree of polymer microspheres of nanometer and submicrometer diameters cannot, however, be directly measured by the classical swelling method, that is used to measure the cross-linking degree of bulk cross-linked polymers [26–30]. We have fortunately established an in situ swelling method to investigate the swelling behavior of cross-linked carboxyl-modified polymer microspheres of submicrometer diameters in a previous report [31]. In this paper, the swelling degrees of nearly monodispersed polymer microspheres with various cross-linking densities were studied using the in situ swelling method. On the other hand, there are few reports, to our knowledge, about medium-dependent color changes of latex crystal films, although similar investigations have been conducted in three-dimensional ordered macroporous materials [7]. We investigated, therefore, the optical spectra of color changes of latex crystal films formed from these microspheres when we filled the interstices in the latex crystal films with different fluid media having various refraction indexes.

2. Experimental

2.1. Materials

4,4’-Isopropylidenediphenol bimethacrylate prepared in our laboratory was used as cross-linker. Styrene and metha-
Table 1 Typical recipes for the preparation of nearly monodispersed microspheres with various contents of cross-linker

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight (g) (reaction temperature 75°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>9.1</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>Cross-linker</td>
<td>0.8</td>
</tr>
<tr>
<td>Potassium persulfate</td>
<td>0.10</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.24</td>
</tr>
<tr>
<td>Deionized water</td>
<td>194.7</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>320</td>
</tr>
<tr>
<td>PDI</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Note: Cross-linker is 4,4′-isopropylidenediphenol bimethacrylate.

Carboxyl-modified polystyrene microspheres with various cross-linking densities were synthesized using a surfactant-free emulsion copolymerization. The details on the preparation and the swelling behavior of polymer microspheres have been previously reported [31]. In this case, the content of other components besides the cross-linker was often held constant in preparing the polymer microspheres. Table 1 shows some typical preparation conditions and samples. For the swelling behavior of the cross-linked polymer microspheres, 0.5 ml of emulsion (0.5 wt% of solid content) was typically dispersed in 3.0 ml of solvent such as ethanol or THF. The swelling degree was determined using the volume method: swelling degree = V₁/V₀, where V₁ is the volume of swollen polymer microspheres and V₀ the volume of unswollen polymer microspheres.

2.3. Preparation of latex crystal films

Latex crystal films were prepared via vertical deposition technology as described elsewhere [32]. A quartz plate or glass slide was immersed vertically into 2.5 ml of as-prepared microsphere emulsion (1.0 wt% solid content) contained in a vial. Then the slide was placed in a desiccator and dried at room temperature. During the deposition process, the capillary force at the meniscus between the substrate and the emulsion induced polymer microspheres to self-assemble into latex crystal films on the quartz plate or glass slide as the dispersing water evaporated.

2.4. Characterization

The average diameter and diameter distribution of the resulting microspheres were determined by Zetasizer 3000 HS. The UV–vis spectrum was recorded using a Shimadzu UV-3100 spectrophotometer. Examinations including FTIR and TEM have revealed that cross-linked carboxyl-modified polystyrene microspheres were prepared and cross-linking had no effect on the monodispersity and the shape of the resulting cross-linked polymer microspheres. We investigated the cross-linked microspheres further with various contents of the cross-linker. Table 1 lists some typical recipes for the preparation of the nearly monodispersed carboxyl-modified polystyrene microspheres with different content of the cross-linker.

We noted that the diameters of the resulting cross-linked microspheres change to a certain extent with the changing content of the cross-linker. There is no significant change in polydispersity index (PDI) or size distribution of the resulting cross-linked microspheres, however. Figure 1 reveals that the diameter of polymer microspheres initially were carried out as follows: the bottom of the plate upon which the latex crystal film deposited was immersed into different fluid media such as water or alcohol, which led to the fluid filling the interstices of the latex crystal film. Finally, the absorbance spectra of the latex crystal films were recorded, or recorded in situ in a quartz cell containing a trace of the liquid mediums. In other words, the sample was placed vertically in a quartz cell containing a trace of liquid medium, and the spectra were recorded in situ.

3. Results and discussion

3.1. Synthesis of cross-linked polymer microspheres with various cross-linked densities

According to our previous work [31], we used 4,4′-isopropylidenediphenol bimethacrylate as a longer chain cross-linker to prepare cross-linked polymer microspheres of narrow size distribution. Examinations including FTIR and TEM have revealed that cross-linked carboxyl-modified polystyrene microspheres were prepared and cross-linking had no effect on the monodispersity and the shape of the resulting cross-linked polymer microspheres. We investigated the cross-linked microspheres further with various contents of the cross-linker. Table 1 lists some typical recipes for the preparation of the nearly monodispersed carboxyl-modified polystyrene microspheres with different content of the cross-linker.

Fig. 1. The plot of the diameter of microspheres versus the content of the cross-linker and the effect of the content of cross-linker on the maximal swelling degree of microspheres (the insert). In the preparation of microspheres, 9.1 g of styrene, 100 g of H₂O, 1.1 g of methacrylic acid, 0.185 g of potassium persulfate, and 0.24 g of NaHCO₃ were used.
increased as the content of the cross-linker increased from 0 to 1.36 mol% (based on monomer). But beyond the 1.36 mol% point, although we continued adding cross-linker up to 3.25 mol%, the diameter of the microspheres no longer varied. This behavior may arise from the number of particles at the end of the nucleation stage determining the ultimate diameter of the microspheres in the microsphere formation mechanism in a surfactant-free emulsion polymerization [33–35]. In our experiment, factors that affect the number of particles at the end of the nucleation stage will therefore affect the microsphere diameter. On one hand, increasing the content of cross-linker improves the rate of nucleation and thus increases the number of primary particles, which leads to a decrease in the diameter of polymer microspheres. On the other hand, because methacrylic acid comonomer is highly soluble in water, oligomers containing methacrylic acid increase their chances of being captured by the existing particles. This effect favors larger microsphere diameters. These two factors would favor the above-mentioned observation that the diameter of the microspheres initially increased as we increased the content of the cross-linker from 0 to 1.36 mol%, and then the diameter did not vary, apparently, despite a further increase of cross-linker from 1.36 to 3.25 mol%.

3.2. The swelling behavior of the cross-linked microspheres

The rate of swelling is inversely proportional to the size of the cross-linked polymer, which induces submicrometer-sized polymer microspheres to respond to the solvents more quickly than bulk cross-linked polymers do. Earlier we reported that the average time required for cross-linked carboxyl-modified polymer microspheres to reach equilibrium was about 60 min or less [31]. In this case, we used the in situ swelling method to study the swelling behavior of cross-linked polymer microspheres with various cross-linking densities. The insert in Fig. 1 indicates that the maximal swelling degrees of the microspheres with various cross-linking densities linearly decrease as the content of the cross-linker increases from 1.36 to 3.25 mol%. This result depends on the fact that increasing the content of cross-linker induces the number of the cross-linking sites to rise, making it difficult for the solvent to diffuse into the microspheres and thereby decreasing the degree of swelling. For example, the number of cross-linking sites is about 73 (over 73 repeat units between cross-linking sites) for microspheres of 1.36 mol% cross-linker, more than 36 of 2.71 mol%, and the maximal swelling degree, 4.03, of the latter is smaller than 6.65 of the former, as shown in Table 2. Table 2 further lists the content of the cross-linker, the swelling degree, and the \( M_e \) (the number-average molecular weight of the network chain between two cross-linking sites) of some typical samples. This result suggests that \( M_e \) depended on the cross-linking density in the polymer microspheres, though the \( M_e \) value measured by this method is typically higher than the theoretical calculated value, which is in agreement with the possibility that there may still be a few double bonds present without a reaction, as verified before. In addition, Table 2 also indicates that as the content of the cross-linker increases, the \( M_e \) of the microspheres decreases.

3.3. Medium-dependent color changes of three-dimensional latex crystals

Some important optical properties such as the stop band and reflected color are caused by Bragg diffraction in the range of visible light by the three-dimensional ordered arrays of as-prepared cross-linked polymer microspheres of narrow size distribution. Figure 2 shows the UV–vis spectral characteristics of latex crystal films made from polymer microspheres 239.1 nm in diameter when the voids were impregnated with water (Fig. 2a) and alcohol (Fig. 2b). After water or alcohol (typically ethanol) diffused into the voids, the stop band peak wavelength red-shifts from 540.0 to 571.7 nm or from 540.0 to 573.4 nm, respectively, followed by succeeding smaller shifts. These numbers are based on the equation of Bragg diffraction [5,8],

\[
m\lambda = \frac{2(n^2 - \sin^2 \theta)}{\sin \theta}^{1/2} D,
\]

where \( m \) is the order of the Bragg diffraction, \( \lambda \) is the wavelength of the absorbance minimum, \( n \) is the average refractive index of the latex crystal films, \( \theta \) is the angle between the normal to the plane of interest and the incident light, and it can affect the stop band wavelength. \( D \) is the diameter of the microsphere [7]. Here \( \theta \) is zero and we assume \( m = 1 \). The average refractive index \( n \) is determined by

\[
n = fn_{\text{latex}} + (1 - f)n_{\text{fluid}},
\]

where \( f \) is the volume fraction of the microsphere, \( n_{\text{latex}} \) is the refractive index of the microsphere, and \( n_{\text{fluid}} \) is the refractive index of the fluid medium.

When the voids of latex crystal films were filled with water or ethanol due to the strong capillary force, according to Eq. (1), \( \lambda \) increases as a result of \( n \) of water or ethanol being larger than that of initial air in the films’ voids. Table 3 lists the different stop band wavelengths when latex crystal films from different-sized microspheres were filled with water or ethanol, respectively. Table 3 shows that the latex crystal films formed from different-sized microspheres refract different colors and their initial shifts are close to the calculated

<table>
<thead>
<tr>
<th>Cross-linker (mol%)</th>
<th>1.36</th>
<th>2.16</th>
<th>2.71</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D ) (unswollen) (nm)</td>
<td>196.6</td>
<td>203.8</td>
<td>203.7</td>
</tr>
<tr>
<td>( D ) (swollen) (nm)</td>
<td>369.2</td>
<td>353.0</td>
<td>324.3</td>
</tr>
<tr>
<td>Swelling degree</td>
<td>6.65</td>
<td>5.19</td>
<td>4.03</td>
</tr>
<tr>
<td>( M_e ) (10^3)</td>
<td>4.53</td>
<td>3.00</td>
<td>1.96</td>
</tr>
<tr>
<td>( M_e ) (10^3)</td>
<td>3.75</td>
<td>2.35</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Note. Here, \( M_e \) is the experimentally calculated value and \( M_e \) is the theoretically calculated value.
Fig. 2. UV–vis spectra of latex crystal films whose voids have been filled with (a) water and (b) ethanol versus the time. (c) The plot of the peak wavelength of latex crystal films filled with water versus the filling time. From 0 to 8 min, the sample was filled with water; from 8 to 12 min, the latex crystal film was dried by letting the water in the voids evaporate; and then after 12 min, it was filled with water again.

Table 3
The absorbance peak wavelength of latex crystal films filled with different fluid media

<table>
<thead>
<tr>
<th></th>
<th>A (188 nm)</th>
<th>B (239.1 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental (nm)</td>
<td>Calculated (nm)</td>
</tr>
<tr>
<td>Air</td>
<td>420.0</td>
<td>418.3</td>
</tr>
<tr>
<td>Water</td>
<td>447.4</td>
<td>444.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>453.0</td>
<td>447.1</td>
</tr>
</tbody>
</table>

Note: Here \( n_{\text{latex}} \) 1.49, \( n_{\text{water}} \) 1.33, \( n_{\text{ethanol}} \) 1.36, and \( n_{\text{air}} \) 1.00, and volume fraction \( (f) \) 0.74 were used in Eqs. (1) and (2).

value according to Eq. (1) when filled with different fluid media. We also found that there are succeeding small shifts following the initial larger shift as shown in Figs. 2a and 2b. For instance, the small shift varying from 571.7 to 592.0 nm for water is larger than that for ethanol, which varies from 573.4 to 579.0 nm. This result may have been due to the movement or the swelling of microspheres in the latex crystal after its voids have been impregnated by water or ethanol. In particular, while water impregnated the voids, the electrostatic force will make the microspheres separate from each other [5,36], which induces the much larger succeeding shift for water than that for ethanol. Figure 2c reveals that spectral position wavelength changes of latex crystal films are a process of impregnating and removing water in the voids. At the beginning of being impregnated with water, the wavelength increases to a larger value, and then no intensive shift occurs. When removing water from the voids by evaporation, the stop peak will return to a certain extent as shown in Fig. 2c. These color changes make it possible for the latex crystal films to function as possible sensors.

4. Summary

Cross-linked polymer microspheres of narrow size distribution with different cross-linking densities were prepared using a surfactant-free emulsion copolymerization. The diameter of these cross-linked polymer microspheres initially increased as the content of cross-linker increased from 0 to 1.36 mol% (based on the total of monomers). Further increasing the content of the cross-linker from 1.36 to 3.25 mol% brought no change in the diameter of the microsphere, however. The swelling of the microspheres measured via the in situ swelling method indicated that the maximal swelling degree of the microspheres with various cross-linking density linearly decreases as a function of the content of the cross-linker. In addition, UV–vis spectra of latex crystal films from the microspheres show that after different fluid media fill the voids of latex crystal films, the stop band peak wavelength triggers the initial larger shift and the succeeding small shift due to the refraction index of the filling media and to the possible further microsphere swelling, respectively.

Acknowledgments

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References