LETTER

Structural Colored Liquid Membrane without Angle Dependence

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ABSTRACT We have demonstrated for the first time that condensed gel particle suspensions in amorphous-like states display structural color with low angle dependence. This finding is in contrast to the common understanding that a periodic dielectric structure is fundamental to photonic band gap (PBG) production, and it validates the theory that a "tight bonding model" that is applicable to semiconductor systems can also be applied to photonic systems. More practically, this structural colored suspension represents a promising new material for the manufacture of reflective full-color displays with a wide viewing angle and nonfading color materials. This liquid system shows promise as a display material because electronic equipment used for display systems can easily be filled with the liquid in the same way that liquid crystals are currently used.

KEYWORDS: structural color • angle dependent • gel particle • amorphous-like state

Multimedia such as television, personal computers, and now cellular telephones with built-in widescreens are invaluable sources of visual information concerning world events and other important matters. People sometimes require access to such information when they are outdoors. In such a situation, a mobile device with a paperlike display would be convenient. Research and development on full-color paperlike display modules for accessing visual information while outdoors have resulted in significant progress (1). Reflective modules that do not suffer from photobleaching, such as photonic crystals composed of periodic dielectric structures, are encouraging candidates for paperlike display technology because they provide good viewability in both bright sunlight and dimly lit environments, with contrast similar to that of newsprint. Moreover, the reflective displays are attractive because they can be very energy-efficient. Recently developed tunable photonic crystals can provide adjustable structural color throughout the entire visible range without the use of color filters (2, 3). However, to design a reflective full-color display with a wide viewing angle, the angle dependence of the structural color used becomes a major issue (4). This is because the structural colors of the photonic crystals, which arise from coherent Bragg optical diffraction, change when observed from different angles.

In this report, we describe how condensed hydrogel particles suspended in an aqueous solution display angle-independent or low-angle-dependent structural colors that are applicable to nonfading color materials and full-color paperlike displays. The structural color-generating mechanism of condensed hydrogel particles suspended in an aqueous solution must be completely different from that of the Bragg diffraction-based mechanism that occurs for most other photonic crystals. The structural colors observed in the suspension do not have the brilliant color observed for gemstone opal, a natural photonic crystal, but they are no less remarkable.

In this experiment, we used submicrometer, charged, spherical hydrogel particles that are weakly cross-linked colloidal particles swollen with water. Gel particles with a narrow particle size distribution can be easily synthesized by emulsion polymerization (5, 6). Because the gel particles in this study exhibited a temperature-responsive volume change, the temperature for all experiments was fixed at 25 °C. With increased particle concentration (polymer content) in the suspension, the optical properties progressively changed, reflecting the aggregated state of the gel particles.

A suspended aqueous solution of gel particles below about 2 wt % polymer is a colorless, low-viscosity liquid. The turbidity of the suspension increases gradually with increased polymer content up to about 2 wt % due to the increase in scattering areas. The gel particles can move around in the suspension and may not form ordered aggregates under these conditions.

Starting at a polymer content of 2 wt %, the suspension suddenly revealed a decrease in turbidity, and it also displayed tunable structural colors and hues depending on the polymer content. The suspension first displayed muted color just after injecting it into a glass cell (see below). If suspensions containing 2−4 wt % polymer remained untouched for a certain period of time, the suspension revealed a brilliant color. This behavior had been observed previously for this type of gel particle suspension (6−11) and is due to the formation of electrostatically stabilized colloidal crystals. The transmission spectra of a gel containing 3.8 wt % polymer, in which gel particles form colloidal crystals, were

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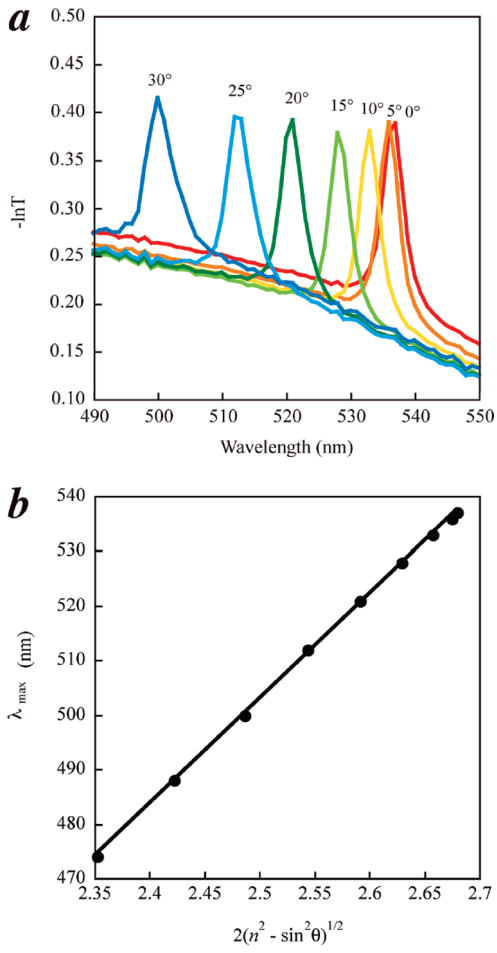

FIGURE 1. (a) Transmission spectra of gel particle suspensions containing 3.8 wt % polymer content measured at various angles at 25 °C. (b) Plots showing λ_{max} of the transmission spectra versus the angle-related parameter, $2(n^2 - \sin^2\theta)^{1/2}$. (c) Confocal micrograph of a suspension containing 3.8 wt % polymer content.

measured at various incident angles to the surface of the quartz thin-layer cell using a UV−visible spectrometer (Figure 1a). The position of the diffraction peak (λ_{max}) shifted continuously from 537 to 474 nm when the angle between the incident light and the detection was changed from 0° to 40°. The Bragg equation modified by Snell's law relates the position of the diffraction peak to the incident angle: $\lambda_{max} = 2(d/m)(n^2 - \sin^2\theta)^{1/2}$ (4, 12), where d is the lattice spacing, m is the order of the Bragg reflection, n is the average refractive index of the suspension, and θ is the angle

FIGURE 2. Optical images of gel particle suspensions with different polymer contents. These images were taken at angles different from the direction of incident light.

measured from the normal position to the plane of the quartz thin-layer cell.

Figure 1b shows a typical experimental result for λ_{max} versus θ. The solid line provides an estimate of the lattice spacing, $d = 192$ nm, assuming $m = 1$ and $n = 1.34$.

Figure 1c shows a confocal microscopy image of the suspension displaying bright structural color. In this image, one can observe that the gel particles are arranged in a hexagonally packed crystalline array. The hexagonal sharp peaks in the two-dimentional Fourier transform of the confocal microscopy image, which is shown in the inset of Figure 1c, confirm the presence of a long-range crystalline order. The particle size, estimated from an image taken with a laser scanning confocal microscope, was 250 nm. On the basis of this diameter, we can conclude that the gel particles must form a face-centered-cubic structure because the crystalline structure exhibits a lattice spacing $d \sim 0.816 \times 250$ nm (the diameter of the gel particles).

In 2−4 wt % suspensions, the gel particles can initially move around in the suspensions immediately after being injected into a glass cell. Over time, the gel particles can eventually form thermodynamically stable non-close-packed or nearly close-packed colloidal crystals, depending on the polymer content and the viscosity of the suspensions. This type of structural colored material possessing a periodic dielectric structure has been widely studied by our research groups (12−17) and others (7−9, 18−23) for optical applications. However, the angle dependence of the structural color observed for these low-percentage polymer colloidal crystals is sometimes unfit for application to nonfading color materials and reflective displays with a wide viewing angle.

In contrast, suspensions with a polymer content of more than 4 wt % and 2−4 wt % suspensions that do not reach thermally equilibrated crystal structures because of the high viscosity exhibited muted but clear colors without angle dependence. Figure 2 shows optical images of freshly prepared gel particle suspensions of 5.6, 4.2, and 2.5 wt %, displaying blue, green, and red, respectively. These colors are constant even when viewed from different directions to the direction of irradiation light. Even gel suspensions with less than 4 wt % displayed angle-independent muted color that appeared a little cloudy just after they were injected into a glass cell, because of the shear melting of the colloidal crystals and the high viscosity of the suspensions. Figure 3a shows the transmission spectra of suspensions with different polymer contents. The smoothly varying background was subtracted from the spectra prior to further analysis because the characteristic spectrum domain corresponding to the

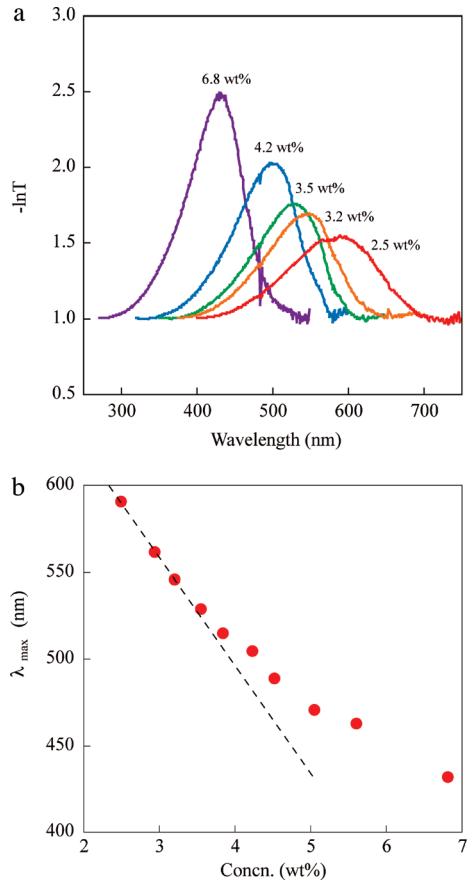

FIGURE 3. (a) Transmission spectra of gel particle suspensions with different polymer contents at 25 °C. (b) Plots showing λ_{max} of the transmission spectra versus the polymer content.

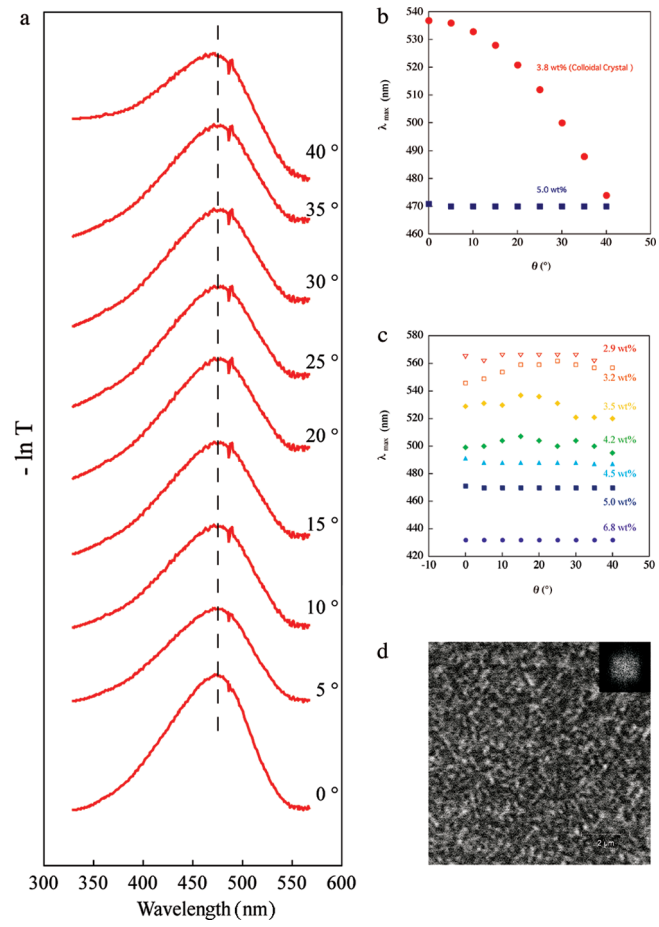

FIGURE 4. (a) Transmission spectra of gel particle suspensions containing 5.0 wt % polymer content measured at various angles at 25 °C. (b) Plots showing λ_{max} of the transmission spectra shown in Figure 1a and Figure 4a versus angle. (c) Plots showing λ_{max} of the transmission spectra for gel particle suspensions with different polymer contents versus the angle at 25 °C. (d) Confocal micrograph of a suspension containing 6.8 wt % polymer content.

appearance of color exhibited a shoulder shape in the unprocessed spectrum. As the polymer content increased, the peak wavelength became shorter. The peak wavelength demonstrated a linear decrease that was proportional to the polymer content up to about 4 wt %, deviating from the line at contents greater than 4 wt % (Figure 3b). This deviation may be due to the elastic rebound arising from bulk deformation of tightly packed gel particles. The highest effective volume fraction is 0.74 for close-packed structures of hard particles, while it can be larger for gel particles due to deformation. The fact that the suspensions became more transparent with increasing polymer content above 4 wt % supports the above-mentioned speculations.

We can interpret this phenomenon based on the occurrence of a phase inversion between the water phase and the gel phase (11). Above a volume fraction of about 0.74, the continuous phase becomes a gel. It follows that the size and number of spangled water droplets in the gel phase decrease with increasing polymer content, which leads to a decrease in the overall scattering area, and the turbidity of the suspension diminishes. Decreased turbidity results in an enhancement in the color of the suspension. It is also worth noting that the gel particles may form a durable, quasi-stable, condensed amorphous-like state, probably because of particle friction. Therefore, in suspensions with higher polymer content, gel particles cannot form thermodynamically stable colloidal crystals.

The transmission spectra of the suspension with 5.0 wt % polymer were measured at various incidences to the sample. The normalized spectra measured at different angles for the suspension are shown in Figure 4a. The position of λ_{max} occurred at 470 nm and did not depend on θ from 0° to 40° (Figure 4b). For all muted structural colors of suspensions above 2 wt % polymer, the positions of λ_{max} were also angle-independent, demonstrating similar angle changes (Figure 4c). Figure 4d shows a confocal microscopy image of 6.8 wt % suspension. The image looks like a disordered arrangement of the gel particles. However, the discrete ring in two-dimentional Fourier transform of the image, which is shown in the inset of Figure 4d, indicates that the periodicity of spatial variation in the refractive index is equivalent in all directions in this plane within the suspension: the gel particles form amorphous-like aggregation in the condensed suspension. Time-resolved pictures (see the Supporting Information) obtained by confocal microscopy provide information about the aggregation structure, which is amorphous-like, and reveal that it varies every second. Thus, it is particularly noteworthy that even the liquid material displays structural color without static ordering. Indeed, the structural color can be observed even when the

suspension is shaking. This result reveals that, if the average distance between particles is relatively constant, a common photonic band gap (PBG) exists in these amorphous-like states regardless of the long-range order. However, the spectral peak observed from the stirred suspension becomes much smaller and broader than that from the static suspension. This may indicate that the motion of the particles in the susupension affects the shape of a PBG.

Since the discovery of the photonic crystal (24, 25), it has been widely believed that the presence of a periodic dielectric structure is a precondition for the presence of a PBG. PBG formation is explained by Bragg scattering of photons due to the periodical dielectric structure. Colloidal crystals composed of submicrometer-sized particles are obviously periodic arrays exhibiting both long- and short-range order, thereby displaying structural color arising from a PBG (4). In contrast, amorphous-like materials such as condensed gel particle suspensions possess only a short-range order lacking periodicity. Therefore, the question arises, how can condensed gel particle suspensions with only short-range order display structural color?

A clue to the answer is provided by recent theoretical reports (26−28). Typically, PBG in photonic crystals is explained as an analogy of the electronic band gap of semiconductors. As above, in most cases, the formation of PBG is largely governed by the Bragg scattering of photons by a periodic lattice. However, there are two approximative models explaining the electronic band gaps in semiconductors: the "free electron model" and the "tight bonding model". If these models are applicable to the explanation of the PBG in photonic systems, the PBG can be formed either by coherent interference of scattered waves from periodic structures such as Bragg diffraction or by bonding and antibonding states of Mie resonances within each particle. According to the "tight-bonding model", two electrons bound to each of the two closely located atoms can couple to form bonding and antibonding states; they each form bonding and antibonding bands, thereby leaving an energy gap between them. This explanation by the "tight-bonding model" does not require the lattice periodicity or long-range order. This indicates that an amorphous structure can exhibit PBGs and display structural color. Moreover, the PBG of the amorphous structure is independent of the angle of incident light. This may be explained in terms of the fact that the change in the refractive index in the amorphous state is isotropic.

In summary, we have demonstrated for the first time that condensed gel particle suspensions in amorphous-like states display structural colors without angle dependence (29). This finding is in contrast to the common understanding that a periodic dielectric structure is fundamental to PBG production, and it validates the theory that a tight-bonding model can be applied to photonic systems. More practically, this structural colored suspension represents a promising new material for the manufacture of reflective full-color displays with a wide viewing angle and nonfading color materials. This liquid system shows promise as a display material because electronic equipment used for display systems can easily be filled with the liquid in the same way that liquid crystals are currently used. To achieve an ideal, reflective, full-color display, the display media must possess high contrast and reflectivity with adequate resolution, as well as tunability that shows a fast response to external stimuli, all of which are present in the polymer gel described herein. Although there are many additional key points inherent to developing an ideal, reflective, full-color display, our finding represents an important milestone (30, 31).

EXPERIMENTAL SECTION

Preparation of Gel Particle Suspensions. *N*-Isopropylacrylamide (Kohjin) as a thermosensitive monomer, acrylic acid (Tokyo Kasei) as an electrolyte monomer, *N*,*N*′-methylenebisacrylamide (Kanto Chemical) as a cross-linker, potassium persulfate (Aldrich) as an initiator, and sodium dodecyl sulfate (Aldrich) as an emulsifying agent were used to prepare the weakly cross-linked gel particles using an emulsion polymerization method in literature reports (5, 6).

Measurements. The transmission spectra of samples in a quartz glass cell with a 1-mm-light path length were obtained using an Ocean Optics USB2000 optical fiber spectrometer with a goniometer. Confocal microscopic images were observed by laser scanning confocal microscopy (Carl Zeiss LSM5 Pascal) with an oil immersion objective lens (NA1.4, Pan-Apochromat).

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Supporting Information Available: Confocal microscopic images of the gel particle suspension and graph of the temperature dependence of the particle diameter measured by dynamic light scattering. This material is available free of charge via the Internet at http://pubs.acs.org.

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