Organic-inorganic hybrid photopolymer with reduced volume shrinkage

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An organic-inorganic hybrid photopolymer containing surface-photoreactive nanoparticles, which exhibits a significant enhancement in optical properties is reported. The photopolymer containing surface-photoreactive nanoparticles showed high diffraction efficiency near 90% and reduced volume shrinkage without affecting the energetic sensitivity and optical quality of the photopolymer. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1954884]

Photopolymerizable materials have gained considerable interest as a promising candidate for the recording medium of holographic data storage devices.[1] Exposure of these materials to light interference pattern initiates a photopolymerization that occurs preferentially in regions of constructive interference. After exposure, the photopolymer contains a periodic pattern as a spatial variation of chemical composition and corresponding variation of refractive index. Since the first photopolymer was reported in 1969,[2] a wide variety of photopolymerizable materials for holographic recording media have been proposed.[3–6] However, their application to the holographic data storage device is severely limited due to high volume shrinkage during holographic recording. The volume shrinkage is closely associated with the entanglement of polymer chains formed during the photopolymerization. Several photopolymer systems have been proposed with reduced volume shrinkage. These photopolymer systems include a hybrid organic-inorganic host based on porous glass,[7] organic-inorganic nanocomposites,[8,9] and the use of monomers capable of cationic ring-opening polymerization.[10] However, these approaches include critical demerits, such as complex synthesis procedures in the cationic ring-opening polymerization-based photopolymer and severe light scattering in the nanoparticle-dispersed nanocomposite-based photopolymer systems. Light scattering seems to be an inevitable phenomenon in these photopolymers because the amount of incorporated nanoparticles reaches 40 wt. % in order to obtain high performance.[11,12] In addition, most of nanoparticle-dispersed photopolymers showed a long induction period at an initial stage of recording.

In this work, we present an organic-inorganic hybrid photopolymer in which surface-photoreactive, organically modified silica nanoparticles are incorporated as a comonomer for the photopolymerization. By incorporating the surface-photoreactive nanoparticles as a comonomer, it is expected that volume shrinkage can be reduced without sacrificing the sensitivity and optical quality of the photopolymer.

The introduction of photoreactive methacrylate units onto silica surface was achieved by the reaction of methacryloyl chloride with hydroxyl groups on the silica (Aerosil® 200) surface, as shown in Fig. 1(a). The conversion of surface hydroxyl group into methacrylate group was confirmed by Fourier transform infrared spectra, and the graft ratio of 2.5 wt. % was determined from thermogravimetric weight

loss analysis. In Fig. 1(b), the structure of photopolymerized polymer and the mechanism of reduction of volume shrinkage due to the rigid silica are conceptually described. Surface-photoreactive nanoparticles introduced in this study are expected to play dual roles with respect to the reduction of volume shrinkage. Due to the rigid silica nanoparticles incorporated in the grating by chemical bonds, the mobility of photopolymerized polymer chains can be reduced, and this can lead to a reduction of free volume change and thus to the volume shrinkage of the recorded gratings. In addition to the contribution to the reduction in the free volume change during photopolymerization, the nanoparticles also contribute to the rigidity enhancement of the medium, which also leads to the reduction of volume shrinkage.

Photopolymers were prepared using poly(methyl-methacrylate-co-methacrylic acid) as a polymer matrix, acryl amide and surface-photoreactive silica nanoparticle as photopolymerizable monomers, triethanolamine (TEA) as a radical generator, and methylene blue (MB). Two different pho-
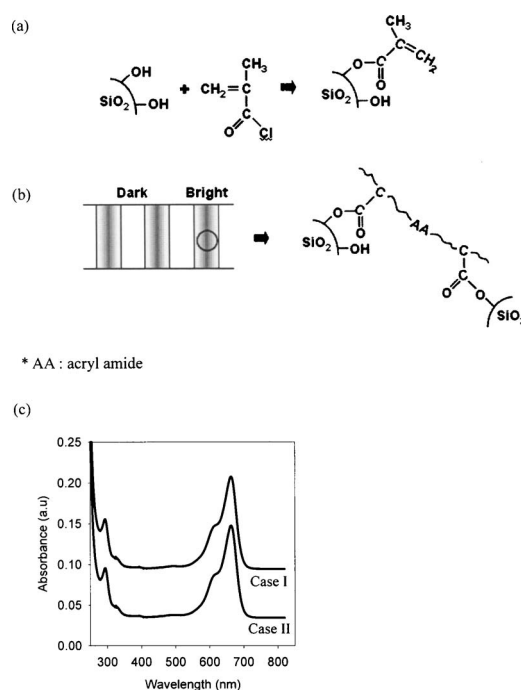

FIG. 1. Molecular structure of a surface-photoreactive silica nanoparticle. (a) Synthetic scheme of a surface-photoreactive silica nanoparticle. (b) Conceptual illustrations on the reduction of volume shrinkage during photopolymerization. (c) UV/Vis spectra for case I and case II.

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TABLE I. Optical properties of photopolymers.

| | Transmittance (%) | Thickness (μm) | Maximum diffraction efficiency (%) | | Refractive index modulation (Δn) | Sensitivity (cm^2/J) | Fractional thickness change |
			η^*	η			
Case I	95	173	73	77	1.385×10^{-3}	1.319×10^{-3}	0.030
Case II	94	164	83	88	2.011×10^{-3}	3.192×10^{-3}	0.025

η^*: Diffraction efficiency defined as $I_{\text{diff}}/I_{\text{in}}$.
η: Diffraction efficiency defined as $I_{\text{diff}}/I_{\text{trans}}+I_{\text{diff}}$.

topolymers were prepared to verify the effect of the surface-photoreactive silica nanoparticles as a comonomer. Case I does not contain surface-photoreactive silica nanoparticles and case II contains surface-photoreactive silica nanoparticles as a comonomer. For the preparation of photopolymers, the polymer matrix:monomer:TEA:MB was dissolved in the ratio 51:25:24:0.06 wt. % in tetrahydrofuran. The mixture was dripped onto glass substrate and left to dry. For case II, silica nanoparticle was incorporated by 1.25 wt. % in the mixture. We prepared ten samples to clarify the reproducibility of our experimental results, and the error range is ±2% for the values of optical transmittance and diffraction efficiency of our photopolymers. Figure 1(c) shows the UV/Vis spectra for case I and case II, and both photopolymers shows maximum absorption at the same wavelength of 633 nm.

First, we investigated the effect of surface-photoreactive silica nanoparticles on the optical quality of photopolymer by measuring the optical transmittance defined by $I_{\text{out}}/I_{\text{in}}$, where I_{out} means light intensity transmitted through the photopolymer and I_{in} means the incident light intensity for the two cases; results are listed in Table I. For the two photopolymers, very high optical transmittance over 90% was obtained. From these results, it is obvious that the incorporated surface-photoreactive nanoparticles do not result in the degradation in the optical quality of photopolymer.

To characterize holographic performance of photopolymers, gratings were recorded in the photopolymers by two mutually coherent writing beams with wavelength of 633 nm and total intensity of 8 mW/cm^2. Figure 2 shows temporal traces of the diffraction efficiencies for case I and case II. The diffraction efficiency η is defined as $I_d/(I_t+I_d)$, where I_d

FIG. 2. Temporal traces of diffraction efficiency of photopolymers: (a) case I and (b) case II.

and I_t are the diffracted and the transmitted light intensities, respectively, so that loss factors such as absorption and light scattering are excluded. To evaluate such loss factors, diffraction efficiency η^* based on incident light intensity was also measured. In the inset of Fig. 2, the slope of the initial increase in the diffraction efficiency until 100 s is steeper for case II than case I. This difference in the initial grating growth rate is originated from the contribution of higher reactivity of methacrylate units grafted on the surface of nanoparticles for case II.

From Figs. 2(a) and 2(b), it is clearly shown that there is a significant increase in the diffraction efficiency with exposure time for case II. Similar phenomena were also reported in previous studies focusing on the nanoparticle-dispersed, binder-free photopolymers,[11,12] and the origin of increase in diffraction efficiency was attributed to a "counterdiffusion" of nanoparticles resulting in the spatially periodic distribution of nanoparticles during holographic exposure. By the term counterdiffusion, Suzuki et al. suggested that when the monomers diffuse into a "bright region" by concentration gradient, the nanoparticles may migrate into a "dark region" during the holographic exposure. However, the explanations based on counter diffusion cannot be applied to our photopolymer because diffusion of the nanoparticles is impossible in the polymer matrix. In our photopolymer, the origin of diffraction efficiency enhancement can be attributed to the additional refractive index modulation via the interfacial hydrogen bonding induced at the hydrophilic surface of silica nanoparticles, which results in a interfacial dipolarity/polarizability change, this presumption was clarified by solvatochromic analysis using Michlers' ketone as a polarity indicator.[13–15] Shifts in λ_{max}, the wavelength at which maximum absorption occurs, of Michlers' ketone were 0 and 8 nm for case I and case II after photopolymerization, respectively. From these results, it could be confirmed that there is an interfacial polarity change via the hydrogen bonding induced between the hydroxyl group at the surface of silica nanoparticles and polar constituents of the photopolymer, and this change in the interfacial dipolarity/polarizability leads to additional refractive index modulation.

Table I summarizes some optical properties of case I and case II. Refractive index modulation (Δn) for the two cases was estimated by Kogelnik's coupled wave theory.[16] It is clear that Δn as well as energetic sensitivity S ($\equiv \Delta n/E$, where E is the exposure fluence) are higher for case II. The sensitivity of case II is higher than that of titanium oxide nanoparticle-dispersed, binder-free photopolymer reported recently.[11] For case II, a much shorter response time of 90 s was obtained for achieving 80% of the maximum diffraction efficiency, while a response time of 160 s was obtained for
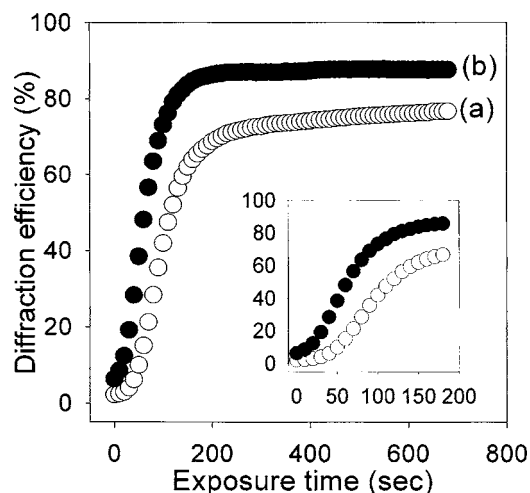
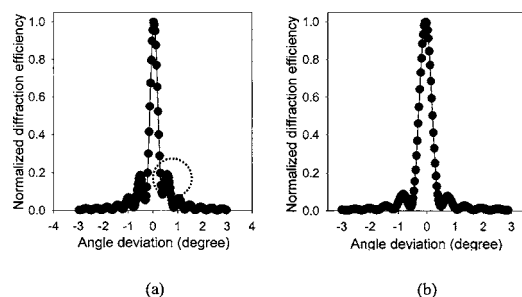FIG. 3. Angular response of photopolymers: (a) case I and (b) case II.

FIG. 4. Confocal fluorescence microscope images of recorded gratings: (a) case I and (b) case II.

case I. It is also noted that the values of η and η^* are similar for case II, indicating that there is negligible light loss due to the Rayleigh scattering from the nanoparticles in case II. We also evaluated the contribution of surface-photoreactive nanoparticles on the volume shrinkage by measuring the fractional thickness change of the photopolymer after holographic exposure, and the results are listed in Table I. The fractional thickness change of photopolymers was measured by a surface profiler system with resolution of 1000 Å and the error range of the fractional thickness change was ±0.001. A lower value of the fractional thickness change ($\Delta d / d$), 0.025, was obtained for case II as compared with 0.030 for case I. From these results, it is concluded that optical properties as well as volume shrinkage of the photopolymer can be enhanced by the introduction of a small amount of surface-photoreactive nanoparticles.

The angular response of the two photopolymers was measured by rotating the photopolymer from the position satisfying the Bragg condition; Fig. 3 shows the angular selectivity of the two photopolymers. For both cases, good Bragg selectivity is observed. However, for case I, uplifted satellite peaks with moderate intensity, compared to case II, are more clearly resolved. The uplift of the first satellite peaks may result from the nonuniformity in grating strength.[17] The origin of nonuniform distribution in refractive index modulation through the depth may include several physical parameters such as thickness difference and wetting characteristics of the photopolymer on glass substrate.[18] Comparing case II with case I, it should be noticed that the uniformity of grating throughout the depth of the photopolymer is also enhanced by the introduction of a small amount of surface-photoreactive nanoparticles.

In Fig. 4, fluorescence microscopic images of two photopolymers are shown. For fluorescence microscopic observation, 0.5 mol % of anthracene moiety was introduced into the carboxylic acid group of polymer matrix. For both cases, about 1 μm of grating spacing was observed and clearer and sharper edge of grating was obtained for case II.
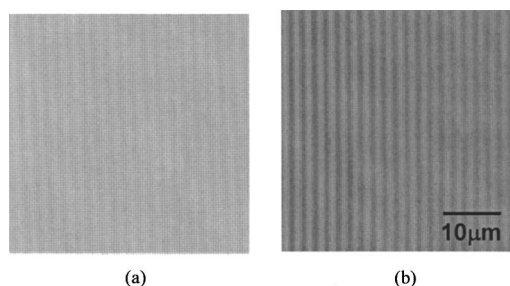
In summary, we have demonstrated an organic-inorganic hybrid photopolymer which shows reduced volume shrinkage and enhanced optical properties by introducing a small amount of nanoparticles with surface-photoreactive units. By incorporating surface-photoreactive nanoparticles, refractive index modulation as well as sensitivity was enhanced without deteriorating the optical quality of photopolymer. The organic-inorganic hybrid photopolymer proposed in this work should be a promising candidate as a recording medium for high-density optical data storage devices.

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