Photopolymerizable nanocomposite photonic materials and their holographic applications in light and neutron optics

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1. Introduction

A nanocomposite photonic material usually consists of a transparent host material incorporating one or more nanometer size materials having different optical properties (1). One very old but well-known example may be colored (or stained) glass and luster ceramics exhibiting physical colors in cultural heritage (2), although they were not photopolymerizable unlike nanocomposite photonic materials to be discussed in this paper. They possess the Maxwell–Garnett composite structure (3) having metallic inclusions that are dispersed in glass and exhibit the unique spectral transmittance/reflectance properties due to the excitation of surface plasmon modes. Other types of nanocomposite photonic materials include Bruggeman and sub-wavelength layered structures (4); the former consists of two interdispersed materials and the latter forms alternating layers of two different materials with their thicknesses much thinner than the optical wavelength of interest. Such nanocomposite structures constructed by, for example, deposition and sputtering methods take advantage of the local field effect and the nanostructuring properties to control the linear optical properties (e.g., the effective refractive index and the absorption spectra), the laser gain properties, and the nonlinear optical properties (4–6). Laser nano-/micro-fabrication and chemical self-assembly methods can also produce nanostructured polymer composites for novel photonic applications (7). Photopolymerizable nanocomposite photonic materials discussed in this paper are different from these nanocomposites in such a way that light-induced mass transfer of photopolymerizable monomer (photopolymer) and nanometer size inclusions (nanoparticles) occurs during holographic exposure. As a result, compositional (density) distributions of the formed polymer and nanoparticles are created holographically, thereby forming multi-dimensional photonic lattice structures in a single-step process. We refer to this type of photonic nanocomposite materials exhibiting programming structure or prescribed morphology (8, 9) by light-induced polymerization as photopolymerizable nanoparticle polymer composites (NPCs) (10) in this paper.

In 1976, the concept of light-induced transfer of an additional photo-insensitive (neutral) or low-reactivity molecular-level organic species in multi-component...
photopolymer was originally suggested by Tomlinson et al. (11) who intended to increase the saturated refractive index modulation amplitude ($\Delta n_{\text{sat}}$) of a refractive index grating. Large values for $\Delta n_{\text{sat}}$ are obviously desirable, for example, to increase diffracted signal power in holographic diffraction elements and recording densities in holographic memories. The principle of the holographic grating formation in such multi-component photopolymer may be described by mutual (two-way) diffusion (12) of two organic species (one with higher reactivity and the other with lower or no reactivity) during spatially inhomogeneous illumination: while monomer with higher reactivity diffuses from the dark to the bright regions, the other with lower or no reactivity counter-diffuses from the bright to the dark regions. When a refractive index difference between these monomer species is set large enough, a refractive index grating with large $\Delta n_{\text{sat}}$ may be induced. Later, other multi-component photopolymer systems incorporated with a variety of neutral molecules as secondary organic species were also proposed. These include high refractive index molecules (e.g. bromonaphthalene, pentachlorodiphenyl, and quinoline), low refractive index ones (e.g. methanol, ethanol, hexane, and acetonitrile) (13–15), and liquid crystals (16, 17).

In 1996, Oliveira et al. (18) proposed a multi-component sol–gel photopolymer system that included inorganic transporting species. The sol–gel process is an interesting route for the preparation of nanocomposites since it allows the low temperature synthesis of materials. In the sol–gel process, such molecular-level inorganic species was formed by the in situ condensation of methacrylic acid (MA)-complexed zirconium isopropoxide $[\text{Zr} (\text{O}^\prime\text{Pr})_4]$ in a matrix material of 3-methacryloxypropyl trimethoxysilane. Since the MA component at the surface of secondary $\text{Zr} (\text{O}^\prime\text{Pr})_4$ species was used to copolymerize with the organic species of the organo-silane (19, 20), monomer containing secondary $\text{Zr} (\text{O}^\prime\text{Pr})_4$ species was found to diffuse from the dark to the bright fringe regions under holographic exposure (18). This way, they demonstrated for the first time the holographic grating formation in the photopolymer by holographic control of densities of inorganic secondary species at molecular level. Later, Vaia et al. also showed holographic control of densities of metallic Au nanoparticles and inorganic meso-/micro-nanoparticles doped in photopolymer (21). del Monte et al. also demonstrated much improved performance of holographic recording in a similar sol–gel multi-component photopolymer, showing $\Delta n_{\text{sat}}$ as large as $1 \times 10^{-2}$ at a probe wavelength of 633 nm and low light scattering loss due to the use of MA:Zr complex at molecular level (22–24).

So far, all-organic binder-based and multi-component photopolymer systems have found various holographic applications such as holographic diffractive optical elements, holographic data storage (HDS), narrowband optical filters, optical interconnects, waveguide couplers, photonic crystals, head-up/head-on displays, and three-dimensional displays (25–34). Among them, holographic photopolymer materials with $\Delta n_{\text{sat}}$ larger than $5 \times 10^{-3}$ and polymerization shrinkage lower than 0.5%, together with high thermal stability, are generally required as holographic recording media for mass storage HDS applications (27). In order to meet such severe demands, Suzuki et al. proposed a new nanocomposite photopolymer system, a photopolymerizable NPC incorporating inorganic oxide TiO$_2$ nanoparticles acting as secondary neutral species at high concentrations, in 2002 (35). Their idea was to use inorganic materials possessing the wide range of refractive indices for a large increase in $\Delta n_{\text{sat}}$ of a recorded volume grating with reduced shrinkage and high thermal stability. For example, refractive indices higher than 3 are even available in semiconductors (36), as compared with polymer refractive indices of the order of, at most, 1.7. Especially, inorganic oxides such as TiO$_2$ and ZrO$_2$ are highly transparent in the visible spectral region and have their refractive indices higher than 2. Incorporation of inorganic nanoparticles with extreme (high or low) refractive indices into photopolymers would give rise to very large $\Delta n_{\text{sat}}$ outside the typical range realized by conventional all-organic photopolymer systems. They showed that the incorporation of TiO$_2$ nanoparticles gave $\Delta n_{\text{sat}}$ as large as $5 \times 10^{-3}$ at a recording wavelength of 532 nm and also contributed to substantive suppression of polymerization shrinkage. Following their demonstration, holographic recording in NPCs employing various types of inorganic nanoparticles has also been reported so far at visible and near-ultraviolet recording wavelengths. These include inorganic nanoparticles (TiO$_2$, SiO$_2$, ZrO$_2$, ZrO$_2$ : Eu$^{3+}$, LaPO$_4$ : Ce$^{3+}$, Tb$^{3+}$, nanozeolites, semiconductor quantum dots (QDs)) (37–64) and organic nanoparticles (65). It was found that, as opposed to Oliveira et al.’s case (18), monomer molecules (neutral nanoparticles) generally diffuse from the dark (bright) to the bright (dark) regions under holographic exposure due to the mutual diffusion of monomer and nanoparticles (66–69). All these reported NPCs employed (meth)acrylate (MA) photopolymers being capable of free radical chain growth polymerization. It was shown that the inclusion of nanoparticles at high concentrations (> 20%) in MA-based NPCs yielded not only an increase in $\Delta n_{\text{sat}}$ but also a substantive reduction in polymerization shrinkage and improved thermal stability at the same time (70). Also, it was shown that measured values for $\Delta n_{\text{sat}}$ and material recording sensitivity ($S$) at a recording and readout wavelength of 532 nm exceeded the minimum required
values of $5 \times 10^{-3}$ and 500 cm/J, respectively, for HDS media (27). However, the reduced shrinkage of volume gratings recorded in MA-based NPCs was still of the order of 1%, larger than the shrinkage criterion (<0.5%) for HDS (27). This shrinkage problem can be relaxed to some extent by the addition of chain transfer agents by which rapid gelation is delayed and thereby shrinkage can be reduced (71, 72). In order to mitigate shrinkage further, we proposed the use of thiol-ene (TE)/thiol-yne (TY) monomers capable of free radical step growth polymerization in NPCs and showed a substantive reduction in shrinkage as low as 0.4% without decreasing $\Delta n_{\text{sat}}$ and $S$ (73–77).

So far, NPCs have been applied to various photonic applications since they possess high degree of material selectivity on nanoparticles and photopolymer for particular target applications. Moreover, one can even utilize the nucleus–neutron interaction (strong force) between holographically assembled nanoparticles in NPCs and incident neutrons to manipulate neutron beams by neutron diffraction from holographic gratings recorded in NPCs. These photonic and neutron optics applications include HDS (78, 79), security holograms (52), holographic sensors (80), nonlinear optics (81), distributed feedback lasers (82, 83), and holographic control of slow-neutron beams (84–87).

This paper is organized as follows: In Section 2, we explain the mechanism of holographic grating formation in NPCs. We discuss the theoretical limit of $\Delta n_{\text{sat}}$ achievable with NPCs. In addition, we describe morphological inspection of recorded holographic gratings by means of physicochemical and optical methods that include transmission/scanning electron microscopes (TEM/SEM), an electron-probe micro-analyzer (EPMA), micro-Raman imaging, an atomic force microscope (AFM), and dynamic optical interferometry. In Section 3, we present the holographic recording properties of various NPC systems. These include NPCs incorporating nanoparticles of metals, inorganic oxides, semiconductors, and organics. Experimental results of holographic recording in these NPC systems are briefly described. In Section 4, we introduce two holographic applications of NPCs: HDS and holographic slow-neutron beam control. In Section 5, we present a conclusion and future directions. We should note that since it is difficult to cover all reported results in this ongoing research field, we mainly describe our results in this review.

2. Holographic grating formation and grating characterization

In this section, we describe the underlying mechanism of holographic grating formation in NPCs in terms of a polymerization-driven mutual diffusion model. The fundamental limit of achievable $\Delta n_{\text{sat}}$ with NPCs is also discussed. Then, we show experimental results of the inspection of formed NPC grating structures in transversal and longitudinal directions by means of both physicochemical and optical methods. These include TEM/SEM, EPMA, micro-Raman imaging, AFM, and dynamic optical interferometry. It is shown that the transversal and longitudinal density distributions of the formed polymer and nanoparticles in a recorded grating are 180° degree phase-shifted to each other with respect to the light intensity interference fringe pattern, as predicted by the model. Note that a recording wavelength used in the grating morphology study shown in this section is 532 nm unless otherwise stated. Details (e.g. the compositions and the holographic recording properties) of NPC systems shown in this section are described in Section 3.

2.1. Mechanism and modeling

As similar to a two-component photopolymer system such as holographic polymer-dispersed liquid crystals (HPDLCs) (88), the holographic grating formation in an NPC may be understood by considering the chemical potential. If one ignores interactions between components of a mixture (monomer, the formed polymer, and nanoparticles), the chemical potential (89) of the $i^{th}$ component of the mixture ($\mu_i$) is approximately written as

$$\mu_i = \mu_i^0 + k_B T \ln \left( \frac{N_i}{\sum_j N_j} \right),$$

where $\mu_i^0$ is the chemical potential of the pure $i^{th}$ component, $N_i$ is the number density of the $i^{th}$ component, and $k_B T$ is the thermal energy. Under thermodynamic equilibrium, $\mu_i$ is constant everywhere in the mixture. Suppose that nanoparticles are uniformly dispersed in monomer capable of, for example, radical chain photopolymerization as shown in Figure 1(a). Spatially non-uniform light illumination produces free radicals by dissociation of initiators and the subsequent reaction of free radicals with monomer leads to the chain polymerization of monomer in the bright regions. As is clear from Equation (1), such polymerization reaction lowers the chemical potential of monomer in the bright regions, leading to migration (diffusion) of monomer from the dark to the bright regions. On the other hand, photo-insensitive nanoparticles experience the counter-diffusion from the bright to the dark regions since they are not consumed and the chemical potential of nanoparticles increases in the bright regions due to the consumption of monomer. This mutual diffusion process essentially continues until the photopolymerization completes. The resultant spatial distribution of nanoparticles is an intensity-inverted
referred to as the mutual diffusion is possible during, at least, the early light-directed mesoscale phase separation and the formed polymer and nanoparticles. (The colour version of this illumination facilitates the mutual diffusion of monomer and nanoparticles of the order of 10 nm or smaller through the bright and dark regions. We note that the diffusion of nanoparticles of the order of 10 nm or smaller in monomer syrup would be possible: the diffusion constant \( D \) of the nanoparticle is given, according to the Stokes–Einstein relation, by \( k_B T / 3 \pi \nu d \), where \( d \) is the diameter of a spherical nanoparticle and \( \nu \) is the viscosity of the monomer syrup. We then find that \( D \approx 1 \times 10^{-8} \text{ cm}^2/\text{s} \) at room temperature for \( d=10 \text{ nm} \) and \( \nu=50 \text{ cP} \) (a typical value of monomer used for holographic recording). This value is within the range of \( D \) reported previously \( (10^{-11} \text{ to } 10^{-7} \text{ cm}^2/\text{s}) \) \( (90, 91) \), suggesting that the mutual diffusion is possible during, at least, the early period of holographic exposure.

Such a grating formation process in an NPC, generally referred to as holographic assembly of nanoparticles \( (66) \) and light-directed mesoscale phase separation \( (92–94) \), may be theoretically modeled, to the first-order approximation, by either a phenomenological approach based on the Fick’s first law or a statistical thermodynamic approach with \( \mu_i \). Indeed, these approaches were used to account for the grating formation dynamics of a two-component photopolymer system in which the size of all constituents is at a molecular level. The former phenomenological approach requires a priori knowledge of mass transfer directions of two components. Nostrum et al. used a static method (i.e. step-by-step calculations of monomer consumption and diffusion in the space–time grid) to simulate the diffusion process that occurs during spatially non-uniform polymerization of a mixture of two monomers with different reactivities \( (95) \). Gyulnazarov et al. \( (96) \) and Karpov et al. \( (97–100) \) formulated the photopolymerization-driven diffusion process under the assumption of the conservation of the volume ratio between two monomers during spatially non-uniform polymerization. Other phenomenological models were also reported to account for the holographic grating formation in HPDLCs \( (101–106) \). All these phenomenological models predict the opposite (mutual) diffusion dynamics of two components (either two types of monomer with different reactivities or reactive monomer and photo-inactive liquid crystal): the most reactive monomer always diffuses toward the bright illuminated regions while the less reactive monomer (or liquid crystal) does toward the dark illuminated regions. However, experimental observations for two monomers with different reactivities sometimes contradicted the above predicted result: both monomers diffuse toward the bright illuminated regions \( (107) \). To explain such discrepancy, Leewis et al. \( (108) \) proposed a statistical thermodynamic model using the Flory–Huggins chemical potential \( (109, 110) \) by which several important physical and chemical effects including reactivity, size, and crosslinking ability of monomer as well as surface tension were taken into account in the analysis. Smirnova et al. also discussed holographic recording in a two-component photopolymer system from a thermodynamical point of view \( (15, 111–114) \). They found that the thermodynamic compatibility of two components (e.g. their solubility parameters) strongly influenced the nature of their phase separation, thereby determining the diffraction properties of a formed holographic grating. More detailed statistical thermodynamic approaches based on the time-dependent Ginzburg–Landau model for photopolymerization-driven mutual diffusion and phase separation in HPDLCs under holographic exposure were also proposed to account for the holographic grating formation and the associated nematic ordering in liquid crystal droplets \( (115–117) \). On the other hand, an NPC system includes photo-insensitive nanoparticles that are much larger than a reactive monomer molecule. Nevertheless, it was found that observed grating buildup dynamics of NPCs could be qualitatively explained by means of Karpov et al.’s phenomenological model \( (118) \). However, in order to explain various experimental observations (e.g. a strong grating-spacing dependence on \( \Delta n_{\text{sat}} \) \( (35, 41, 47, 71, 72, 74, 76) \)) and to make the material optimization possible for specific applications, one needs to establish a more appropriate statistical thermodynamic model that accurately takes the interaction of nanoparticles with monomer and the formed polymer \( (119) \) into account.

Figure 1. Schematic of holographic grating formation in an NPC film. (a) Constituents (monomer and nanoparticles) are uniformly dispersed before exposure. (b) Spatially inhomogeneous light illumination facilitates the mutual diffusion of monomer and nanoparticles, resulting in the phase-separated distributions of the formed polymer and nanoparticles. (The colour version of this figure is included in the online version of the journal.)

2.2. Fundamental limit of the refractive index modulation amplitude

As similar to the discussion by Tomlinson and Chandross \( (120) \) for all-organic binder-based photopolymer,
the theoretical upper limit of $\Delta n_{\text{sat}}$ for NPCs may be estimated by the following simple argument. The effective refractive index ($n$) of a mixture of physically and chemically different components is given by the Lorentz–Lorenz formula,

$$n^2 - 1 = \sum_i \frac{\rho_i A_i}{W_i},$$

where $\rho_i$, $A_i$, and $W_i$ are the density, the molar refractivity, and the molar weight of the $i$th component in the mixture, respectively. A change in $n$ caused by small changes in $\rho_i$ ($\equiv \rho$) and $A_i$ ($\equiv A$) due to polymerization for the $i$th component can be easily obtained by differentiating Equation (2) with respect to $\rho_i$ and $A_i$, resulting in the following overall net change in $n$ ($\Delta n_{\text{net}}$):

$$\Delta n_{\text{net}} = \frac{(n^2 - 1)(n^2 + 2)}{12n} \left( \frac{\Delta A}{A} + \frac{\Delta \rho}{\rho} \right).$$

It can be seen that $\Delta n_{\text{net}}$ is induced by the fractional changes in $A$ through the photochromic/orientational effect of molecules and in $\rho$ through any density changes such as polymerization and spatial mass transport of components. Because $n$ generally varies from 1.4 to 1.7 for typical organic materials, the prefactor $(n^2 - 1)(n^2 + 2)/12n$ in the right-hand side of Equation (3) takes a value between 0.23 and 0.45. On the other hand, $\Delta A/A$ and $\Delta \rho/\rho$ (particularly due to polymerization) may be at most equal to or lower than 0.2 and 0.3, respectively, for typical organic materials (120). Using these values, we find $\Delta n_{\text{net}}$ to be between 0.069 and 0.135. Then, we find the corresponding first-order sinusoidal component of $\Delta n_{\text{net}}$ (i.e. $\Delta n_{\text{sat}}$) for the rectangular modulation in space, which is given by $\Delta n_{\text{net}} \sin (r\pi)/r$ ($r$ is the duty ratio of the rectangular modulation), to be $0.022 \sim 0.043$ at $r = 0.5$ (the 50:50 duty ratio) for all-organic binder-based photopolymers.

This upper limit of $\Delta n_{\text{sat}}$ may be overcome by introducing a two-component photopolymer system by which $\Delta \rho/\rho$ can be enhanced by mass transport, as suggested by Tomlinson and Chandross (120):

One can alter the relative concentrations of the various components of the sample while leaving the overall density unchanged. This requires both the addition and the removal of material. Of course, to get a large change in refractive index, one must alter the relative concentrations of components that have significantly different refractivities.

Such enhancement by mass transport of monomer and nanoparticles having different refractive indices can be realized by holographic assembly of nanoparticles as shown in Figure 1. In this case, $\Delta n_{\text{sat}}$ for rectangularly modulated densities of the formed polymer and nanoparticles is given by, as similar to HPDLC gratings (121),

$$\Delta n_{\text{sat}} = \frac{2}{\pi} (n_n - n_p) \Delta f \sin (r\pi),$$

where the assumption of the two incompressible component species is made, $n_n$ ($n_p$) is the refractive indices of a nanoparticle (the formed polymer), and $\Delta f$ is a change in the volume fractions of dispersed nanoparticles in the dark and the bright regions during holographic exposure (21, 35). It should be noted that Equation (4) is valid only for the low concentration limit of nanoparticles dispersed in monomer. It is found that $\Delta n_{\text{sat}}$ is 0.066 for $n_n = 2.55$ (a bulk refractive index of TiO$_2$), $n_p = 1.52$ (a typical value for acrylate photopolymer), $\Delta f = 0.1$ and $r=0.5$. It is larger than that for all-organic binder-based photopolymers, showing the usefulness of NPCs for the enhancement of $\Delta n_{\text{sat}}$.

2.3. Inspection of holographic grating structures

2.3.1. TEM and SEM analyses

The morphology of transmission and reflection gratings recorded in conventional all-organic photopolymers and HPDLCs was examined by chemical pre-processing of all-organic grating samples prior to TEM and SEM measurements (88, 89, 122). It should be easier to observe inorganic nanoparticle distributions embedded in an NPC grating sample without any chemical pre-processing after...
recording because of the large electron scattering cross section of inorganic nanoparticles (21, 65–67). Figure 2(a) and (b) shows 2D TEM images of the cross sections of plane-wave transmission gratings recorded at grating spacing of 1 μm in NPC film samples incorporating 34 vol.% SiO₂ nanoparticles and 34 vol.% hyperbranched polymer (HBP) organic nanoparticles, respectively. These films were sliced (parallel to a substrate surface) into ultrathin sections. The chemical treatment with RuO₄ solution was made beforehand in the latter sample in order to stain HBP organic nanoparticles for the TEM observation (65). It can be seen that the nanoparticle distributions are periodic in the transversal direction. These results show that, as described in Section 2.1, uniformly dispersed nanoparticles (regardless of inorganic and organic) redistribute under holographic exposure to follow the light intensity interference fringe pattern. It is also possible to visualize the distribution of nanoparticles in a recorded grating by a SEM method (67). In this case, however, the contrast of a SEM image is reversed with respect to that of a TEM image since a focused electron beam is predominantly scattered off by nanoparticles in the TEM measurement.

2.3.2. EPMA analysis

The morphology of distributions of the formed polymer and nanoparticles patterned in a recorded NPC grating can also be examined by a 2D elemental analysis using EPMA (67, 69). Figure 3 shows 2D images of the cross sections of a plane-wave transmission grating recorded at grating spacing of 2 μm in an NPC film sample incorporating 34 vol.% SiO₂ nanoparticles (67). In this EPMA analysis, it was possible to identify the distribution of the formed polymer using S and C atoms as label elements since the monomer contained S atoms as well as C atoms. Likewise, the distribution of SiO₂ nanoparticles could be identified from spatial distributions of Si and O atoms acting as the other label elements. The scanned areas were 10 and 5 μm in horizontal and vertical directions, respectively, with image pixels of 256 × 128. The bright regions seen in a secondary electron image [Figure 3(a)] correspond to the reflection of secondary electrons predominantly from Si atoms because of their large scattering cross section as compared to those of other elements. Note that since the induced surface corrugation of the sample after holographic exposure is a few nm as shown later in the AFM analysis, the secondary electron image is due, mostly, to backscattering from SiO₂ nanoparticles embedded in the formed polymer within approximately 1 μm penetration depth of the NPC film sample (67). It can be seen that the 2D transversal distributions of Si atoms [Figure 3(b)] and S atoms [Figure 3(c)] are out of phase. This result indicates that monomer and nanoparticles transport in the opposite direction to each other during holographic exposure, confirming the photopolymerization-driven mutual diffusion model described in Section 2.1.

Figure 4 shows transversal distributions of C and S atoms (the formed polymer) and O and Si atoms (SiO₂ nanoparticles) in four NPC plane-wave transmission gratings recorded at four different exposure times. Each grating was post-exposed by uniform incoherent light to fix the distributions of the formed polymer and SiO₂ nanoparticles. It can be seen that the spatial modulation of constituents’ density distributions increases with an increase in exposure time. In Figure 4, the partial drop in the induced Δn at recording times longer than 30 s was seen in the buildup dynamics of Δn. This trend was caused by the polymerization in the dark regions of the light intensity interference fringe pattern at longer exposure times, indicating a decrease in the spatial modulation of constituents’ density distributions at longer exposure times. The observed result shows that the distributions of the formed polymer and nanoparticles are out of phase with each other during and after holographic exposure.
Figure 4. EPMA images of C and S atoms (the formed polymer) and Si and O atoms (SiO$_2$ nanoparticles) in a plane-wave grating induced in an NPC film incorporating 34 vol.% SiO$_2$ nanoparticles at four different exposure times (above). The recorded grating spacing ($\Lambda$) was 10 $\mu$m. Buildup dynamics of $\Delta n$ as a function of recording time (below). (The colour version of this figure is included in the online version of the journal.)

Figure 5. (a) Transversal line scan density profiles of the formed polymer and ZrO$_2$ nanoparticles (above). Transversal density mapping of the ratio of the Raman spectral intensity data for ZrO$_2$ nanoparticles to that for the formed polymer in a holographic grating at grating spacing of 10 $\mu$m (below). (b) Longitudinal density mapping of the ratio of the Raman spectral intensity data for ZrO$_2$ nanoparticles to that for the formed polymer in a holographic grating at grating spacing of 10 $\mu$m (left). The corresponding line scan traces along the depth direction from the bottom to the top at grating spacing of 10 $\mu$m (right). (The colour version of this figure is included in the online version of the journal.)

2.3.3. Micro-Raman analysis

3D imaging of elemental distributions in an NPC grating was conducted by means of a confocal scanning Raman microscope (69). It enables us to perform non-destructive examination of the formed polymer and nanoparticle distributions along both the transversal (parallel to the film surface) and longitudinal (parallel to the film thickness) directions of a recorded NPC grating at micron-order resolution without sample pretreatment. Figure 5(a) shows transversal line scan density profiles of the formed polymer and ZrO$_2$ nanoparticles (above) and the transversal density mapping of the ratio of the Raman spectral intensity data for ZrO$_2$ nanoparticles to that for the formed polymer (below) embedded in a plane-wave transmission grating recorded at grating spacing of 10 $\mu$m (69). It can be seen that the assembly of ZrO$_2$ nanoparticles is periodically distributed and is out of phase with that of the formed polymer. This result is consistent with the EPMA measurement results shown earlier. Figure 5(b) shows longitudinal density mapping...
Figure 6. AFM images of surface morphology of plane-wave transmission gratings recorded in NPC film samples incorporating (a) 11 vol.% SiO₂ and (b) 34 vol.% HPB organic nanoparticles. Grating spacing of the examined samples was 1 µm. (The colour version of this figure is included in the online version of the journal.)

of the ratio of the Raman spectral intensity data for ZrO₂ nanoparticles to those for the formed polymer (left) and the corresponding line scan traces along the depth direction measured from the bottom to the top (right) for the same NPC grating sample. It can be seen that the spatial modulation of the density distribution tends to decrease along the depth direction due mainly to the aberration of the imaging system through a 1 mm-thick glass substrate. The details of these measurements are described in (69).

2.3.4. AFM analysis
Any surface corrugation of a recorded grating may take place as a result of a volume change caused by mass transfer of monomer and nanoparticles during holographic exposure. Indeed, the observation of such a surface relief grating structure on an HPDLC film surface was reported (123). Figure 6 illustrates AFM images showing the surface morphology of plane-wave transmission gratings recorded in NPC film samples incorporating 11 vol.% SiO₂ [Figure 6(a)] and 34 vol.% HPB [Figure 6(b)] nanoparticles, respectively. Note that these NPC film samples were coverplated during holographic recording. It can be seen that small corrugation appears on these sample surfaces. However, average heights of the corrugation (i.e. the surface-relief grating) are of the order of 1 nm, much lower than 27 nm height for a coverplated sample recorded in all-organic single-component photopolymer (124) in which only monomer moves from the dark to the bright regions so that there is no volume compensation by the mutual diffusion of nanoparticles transporting from the bright to the dark regions. Therefore, the contribution of such a surface-relief grating to diffraction is negligible compared to a recorded volume grating possessing Δn_{sat} being of the order of 0.001 or larger for an NPC film with the thickness of tens of µm or thicker. This observation also indicates that the periodic assembly of nanoparticles is attributed to the mass transfer of nanoparticles during holographic exposure: the volume change in the bright regions into which monomer diffusion is compensated for by the counter-diffusion of nanoparticles from the bright to the dark regions, so that a difference in the total volume concentration between the bright and the dark regions is minimized.

2.3.5. Optical characterization
As discussed in the previous subsection, the counter-diffusion of monomer and nanoparticles would take place in an NPC film during holographic exposure. This means that if nanoparticles (monomer) move from the bright (dark) to the dark (bright) regions of the light intensity interference fringe pattern during holographic exposure, a phase shift (Φ) between the light intensity interference fringe pattern and the induced refractive index grating would be 0° (180°) when n_n is lower (higher) than n_p. It follows immediately that the transporting direction of monomer and nanoparticles under holographic exposure can be determined by measuring Φ optically. Such a measurement was performed by Suzuki and Tomita (68) who modified Kondilenko et al.’s running fringe method used for photorefractive crystals (125). Real-time evolution of Φ was measured by analyzing temporal changes in transmitted intensities of two recording beams as a function of the external phase shift that was intentionally introduced in one of the recording beams during holographic recording. This way, temporal evolution of Δn and Φ was measured simultaneously. In order to examine the transporting direction of nanoparticles, two types of NPCs were prepared: one incorporating TiO₂ nanoparticles (n_n > n_p) and the other incorporating SiO₂ nanoparticles (n_n < n_p).

Figure 7 shows measured results for NPC films incorporating 15 vol.% TiO₂ [Figure 7(a)] and 34 vol.% SiO₂ [Figure 7(b)] nanoparticles, respectively, at grating spacing of 1 µm and a recording intensity of 100 mW/cm².
Under this recording condition, the photopolymerization-driven diffusion process plays a major role in the grating formation. It can be seen that \( \Phi \) is approximately 180° (i.e. \( \Delta n \) is the highest in the dark regions) for the NPC film incorporating TiO\(_2\) nanoparticles, while it is 0° (i.e. \( \Delta n \) is the highest in the bright regions) for the NPC film incorporating SiO\(_2\) nanoparticles. These results indicate that nanoparticles indeed experience the counter-diffusion from the bright to the dark regions under holographic exposure, confirming again the validity of the photopolymerization-driven mutual diffusion model and the definitive role of nanoparticles as a mobile component that increases \( \Delta n \) in holographic recording. The details of this measurement method and results are described in (68).

### 2.4. Characterization of a refractive index grating by diffraction

A holographically recorded unslanted transmission grating with its thickness \( d \) along, say, the \( z \) direction is a static 1D periodic structure along the \( x \) direction. It is characterized by its refractive index profile, which can be expanded in a Fourier series due to the periodicity, as given by

\[
n(x, z) = n_0 + \sum_{j=1}^{\infty} \Delta n_j \cos\left(\frac{2\pi x}{\Lambda} + \Phi\right) \quad \text{for} \quad -d/2 \leq z \leq d/2,
\]

where \( n_0 \) is the background (average) refractive index of a recording medium, \( \Delta n_j \) is the refractive index modulation amplitude at the \( j \)th component, \( \Lambda \) is the grating spacing, and \( \Phi \) is the phase shift defined in Section 2.3.5. In an ideal holographic recording material, the light intensity pattern is perfectly mapped onto the refractive index profile. Therefore, the simplest case to be considered is a sinusoidal interference pattern illuminating a photopolymer material. Such an ideal case of a sinusoidal refractive index profile may not be usually realized for photopolymer materials including NPCs (see, e.g. Figure 5) since the profile is strongly dependent on the ratio of monomer diffusion to polymerization rates (118, 126). Nevertheless, it would be a good approximation to consider only the two lowest order Fourier components \( (n_0 \equiv n, \Delta n_1 \equiv \Delta n_{\text{sat}}) \) since a first-order diffracted signal from a volume grating is still the main contribution and comes from diffraction by \( \Delta n_{\text{sat}} \) recorded in NPCs. Thus, an NPC grating of interest can be characterized by \( n, \Delta n_{\text{sat}}, \Lambda, \) and \( d \).

To describe diffraction of light and (slow) neutron beams from periodic media characterized by Equation (5), one is required to solve the wave equation. In solid-state physics, the corresponding solutions are the well-known Bloch waves in the band theory of electrons (127, 128). A prevalent and fully equivalent approach in light optics is the so-called coupled-wave analysis. A number of related theories have been reported to take account for various simple cases in diffraction (129). These include: (1) a large number of high-order diffracted waves (130) and (2) only two waves (transmitted and first-order diffracted waves) to propagate (131–136) as sole waves in periodic media, respectively. In its rigorous counterpart model, coined as the rigorous coupled-wave analysis (RCWA)(137, 138), an infinite set of second-order differential equations are solved, subject to the boundary conditions at \( z = \pm d/2 \). It covers all cases including two cases mentioned above and allows to discriminate between three diffraction regimes: (1) the Raman–Nath diffraction regime (130, 139), (2) the Bragg diffraction regime (131, 140), and (3) the RCWA diffraction regime, respectively (141). There are basically four parameters involved to determine one of the diffraction regimes: \( \Lambda, \Delta n_{\text{sat}}, d, \) and the wavelength (\( \lambda \)) of an incident beam. Specifically, the following combination of inequalities has to be satisfied simultaneously for each diffraction regime (139–141):

\[
\frac{n_d}{\lambda} - \frac{d}{\Lambda} \leq \frac{\Delta n_{\text{sat}}}{\lambda} \leq \frac{n_s}{\lambda} - \frac{d}{\Lambda},
\]

where \( \frac{n_d}{\lambda} \) and \( \frac{n_s}{\lambda} \) are the transmission and reflection limits of the material, respectively.

\[\text{Figure 7. Temporal evolution of } \Delta n \quad \text{and the phase shift } \Phi \quad \text{for NPC films incorporating (a) TiO}_2 \quad \text{and (b) SiO}_2 \quad \text{nanoparticles in which a transmission plane-wave grating of 1 \( \mu \)m spacing was recorded in each NPC film by two mutually coherent beams at a wavelength of 532 nm.}\]
where \( Q' = Q / \cos \theta_B \) in which \( Q \) and \( \theta_B \) are the Klein–Cook parameter and an incident Bragg angle in a medium, respectively, given by

\[
Q = \frac{2\pi \lambda d}{n\Lambda^2},
\]

\[
\theta_B = \cos^{-1} \sqrt{1 - (\lambda/(2n\Lambda))^2},
\]

and \( \nu \) is the grating strength parameter given by

\[
\nu = \frac{\pi d \Delta n_{sat}}{\lambda \sqrt{1 - (\lambda/(2n\Lambda))^2}}. \tag{11}
\]

For our various NPC gratings to be described in Section 3, the parameters \( (n, \Delta n_{sat}, \Lambda, d, \lambda) \) are more or less 1.5, \( 1 \times 10^{-2} \), 1 \( \mu \text{m} \), 20–50, and 0.532 \( \mu \text{m} \), respectively, for light beams. Then, it is found that 43 \( \leq Q' \leq 108 \) and 1.2 \( \leq \nu \leq 3 \), fulfill both inequalities of Equation (7) for the Bragg diffraction regime. Therefore, it is legitimate to regard diffraction from NPC gratings as the Bragg diffraction regime in light diffraction experiments described in this paper. They are also categorized as thick (volume) gratings since \( d/\Lambda > 10 \) (141). In this case, the diffraction efficiency \( (\eta) \) (131) is given by

\[
\eta = \sin^2 \nu. \tag{12}
\]

Therefore, one can experimentally determine \( \Delta n_{sat} \) from measured data for \( \eta \) together with Equation (12). The detailed extraction procedure is described in Refs. (41) and (50). On the other hand, the RCWA diffraction regime has to be taken into account in neutron diffraction experiments described in Section 4.2 since slow neutron wavelengths are two orders of magnitude shorter than visible light wavelengths (142). Discussions on this point will be made in Section 4.2.

3. Photopolymerizable NPC systems and their holographic recording properties

In this section, we describe various types of photopolymerizable NPC systems and their holographic recording properties. These NPC systems can be classified by dispersed nanometer-scale particles (i.e. inorganic and organic nanoparticles) and by various photopolymerization mechanisms that include free radical-mediated chain growth, step growth, and cationic ring-opening photopolymerization. Although these NPC systems must be particularly designed for target applications, many of the reported NPC systems have employed MA monomers being capable of free radical-mediated chain growth photopolymerization. Experimental results are also described briefly. For their details, readers are encouraged to consult the cited references here.

3.1. Inorganic NPC systems

3.1.1. Use of free radical-mediated chain growth polymerization

3.1.1.1. Metallic nanoparticle dispersion. Since refractive indices of metallic nanoparticles (e.g. Au, Ag, and Cu) are lower than unity in the visible (36), one can expect large refractive index differences between the formed polymer and nanoparticles and therefore large values for \( \Delta n_{sat} \) as shown in Equation (4). Vaia et al. reported one-step micrometer-scale organization (assembly) of Au nanoparticles (5 nm in core diameter) and other larger particles [polystyrene latex mesoparticles (260 nm in diameter) and micron-scale layered silicate powder] using holographic photopolymerization (21). Their motivation was to realize non-sequential one-step patterning of generic particles (regardless of their shape, size, and composition) into complex patterns on multiple length scales and arbitrary orientation. They demonstrated volume holographic recording for the first time in Au nanoparticle-dispersed NPC films consisting of a mixture of 50 wt.% ethoxylate trimethylpropane triacrylate ester and 17 wt.% penta-acrylate as an acrylate monomer blend, Rose Bengal and triethylamine as a photoinitiator system, and Au nanoparticles at concentrations between 0–5 wt.% . A holographic plane-wave grating was recorded by two 532 nm beams at grating spacing of approximately 0.8 \( \mu \text{m} \). It was read by a 633 nm beam to evaluate the net diffraction efficiency (defined as the ratio of the first-order diffracted power to the incident one) and the morphology of the grating. The net diffraction efficiency was 33% for a 6.75 \( \mu \text{m} \)-thick NPC film. They observed that the recorded grating was stable over long time periods of the order of months. A TEM measurement confirmed that Au nanoparticles embedded in the recorded plane-wave grating were periodically assembled according to the exposed light pattern. Later, Goldenberg et al. reported volume holographic recording in acrylate-based NPCs incorporating Au nanoparticles (1.5–3 nm in core diameter) at a recording wavelength of 365 nm (143). They found \( \Delta n_{sat} \) as large as 7.3 \( \times 10^{-3} \) at a probe wavelength of 633 nm and at grating spacing of 0.98 \( \mu \text{m} \) for a \( \sim 20 \mu \text{m} \)-thick NPC volume grating incorporating 1.5 wt.% Au nanoparticles. They concluded...
that such large refractive index modulation was caused not only by the mass transport of Au nanoparticles but also mostly by the increase in the segregation of the polymer-forming phase between the grating planes (i.e. the occurrence of the surface relief grating up to 400-nm height at grating spacing of 4.2 μm) because of the reactivity of Au nanoparticles during photopolymerization. It was also reported that mixed (refractive and absorptive) gratings could be induced in Au nanoparticle-dispersed phenanthrenquinone-PMMA photopolymer (144, 145). An effect of Au nanoparticle diameter ranging from 12 to 26 nm on the holographic properties was also reported for PVA/acylamide-based NPCs (146). Since Au nanoparticles embedded in polymer exhibit substantive UV and plasmonic absorption around 500 nm, the uniform dispersion of Au nanoparticles at high concentrations (tens of vol.%) in a thick film is difficult to handle in practice. These factors may severely limit the use of metallic nanoparticles for holographic applications. On the other hand, Ag nanoparticles-dispersed NPCs generally possess low absorption in the visible. Smirnova et al. (147) reported a new method of patterning the periodic distribution of Ag nanoparticles in a polymer matrix, which consisted of two steps: the ordering of photopolymer composites and the optically or thermally induced reduction of Ag nanoparticles from the precursor AgNO3 under holographic exposure. They showed that Δn_sat as large as 1.42 × 10^-2 could be achieved at recording and probe wavelengths of 488 and 633 nm, respectively. They also confirmed holographic assembly of Ag nanoparticles in the polymer matrix by TEM measurements. Balan et al. (148) reported holographic recording in an NPC film containing Ag nanoparticles that were generated in situ by means of a photochemically assisted synthesis. They showed a clear-cut segregation of Ag nanoparticles between dark and bright regions of the light intensity interference fringe pattern.

3.1.1.2. TiO2 nanoparticle dispersion. Since NPCs incorporating oxide nanoparticles are generally transparent in the visible, they are useful for photonic applications. Suzuki et al. reported the first demonstration of volume holographic recording in NPC films incorporating oxide TiO2 nanoparticles (15 nm) having the high bulk refractive index of 2.55 (35). TiO2 nanoparticles were prepared in vitro by gas phase reaction and were in the rutile phase. TiO2 nanoparticles sol in a mixed solution of methyl isobutyl ketone and n-butyl alcohol was dispersed to methacrylate monomer, 2-methyl-acrylic acid 3-(2-methyl-acryloyloxymethyl)-octahydro-4,7-methano-iden-5-ylmethyl ester. Titanocene photoinitiator was also added in 1 wt.% with respect to the monomer, providing the photosensitivity in the green. An unslanted transmission plane-wave grating was recorded in the 50 μm-thick NPC film by two s-polarized beams at 532 nm and its grating buildup dynamics were monitored by a single beam at 633 nm. They showed that Δn_sat as large as 5 × 10^-3 was obtained at grating spacing of 1 μm for the NPC incorporating 15 vol.% TiO2 nanoparticles. They also found that, as seen in Figure 8, while Δn_sat monotonically increased as large as 8.2 × 10^-3 up to grating spacing of 2 μm (at which the Q parameter (149) still exceeds 20, indicating the operation in the Bragg diffraction regime), it decreased with a decrease in grating spacing. Although such a high spatial frequency roll-off of Δn_sat is found in all-organic binder-based photopolymer systems due to the non-local chain growth (150) or the out diffusion of low molecular weight monomer radicals (151), it is typical for multi-component photopolymer systems including NPCs (41, 47, 62, 65, 71) and HPDLCs (104, 105, 117), too. In addition, they demonstrated the substantive shrinkage mitigation by the dispersion of TiO2 nanoparticles: the out-of-plane fractional thickness change (σ) (152) of recorded volume gratings decreased from 8% without to 2.9% with 15 vol.% TiO2 nanoparticles. Later, Sánchez et al. (37) and Sakhno et al. (38) also reported volume holographic recording at UV wavelengths (351 and 364 nm) in acrylate monomer-based NPCs incorporating surface-modified TiO2 nanoparticles. They obtained values for Δn_sat as large as 1.55 × 10^-2 (37) and 1.65 × 10^-2 (38) evaluated at a probe wavelength of 633 nm with 30 and 25 wt% dispersion of TiO2 nanoparticles, respectively.

3.1.1.3. ZrO2 nanoparticle dispersion. Volume holographic recording in NPCs using another high refractive index material, ZrO2 nanoparticles (3 nm in core diameter) having the high bulk refractive index of 2.1,
was also reported (47, 50, 71, 72). They were prepared by liquid-phase synthesis and were dissolved in toluene solution. Such ZrO$_2$ sol was dispersed to acrylate monomer, 2-propenoic acid, (octahydro-4,7-methano-1H-indene-2,5-diy|bis(methylene) ester. Titanocene photoinitiator was also added in 1 wt% with respect to the monomer. As seen in Figure 9, the dispersion of 35 vol.% ZrO$_2$ nanoparticles with improved surface treatment, in addition to the inclusion of hydrogen donor and acceptor agents as a photosensitizer system (N-phenylglycine and 3,3'-bismethoxycarbonyl-4,4'-tert-butyl peroxycarbonyl benzophenone) (50), could increase $\Delta n_{sat}$ and $S$ by factors of approximately 2 and 9, respectively, at a recording intensity of 10 mW/cm$^2$, as compared with $3.9 \times 10^{-3}$ and 1000 cm$^{-1}$ of the first demonstration of volume holographic recording in NPCs at the optimum ZrO$_2$ concentration of 15 vol.% (47). Thermal stability could also be significantly improved by adding ZrO$_2$ nanoparticles (70). Furthermore, $\Delta n_{sat}$ could be increased to as large as $1.6 \times 10^{-2}$ by incorporating chain-transferring thiols (71, 72). At the same time, the spatial frequency response of recorded gratings was improved and $\sigma$ was also reduced to as low as 1%. In addition, remarkable suppression of light scattering loss was seen due to the small size of ZrO$_2$ nanoparticles. It was found that a 40 $\mu$m-thick NPC film with the ZrO$_2$ nanoparticle concentration of 15 vol.% had the scattering loss lower than 1% at a wavelength of 532 nm. This result means a more than 20-fold scattering noise reduction as compared with those of NPCs incorporating TiO$_2$ nanoparticles (35, 37). The result is also comparable to that of NPCs incorporating SiO$_2$ nanoparticles (41) and the sol–gel photopolymer with MA:Zr complex species (22–24). When the scattering loss was converted to the estimated scattering coefficient, it was 1.6 cm$^{-1}$ for NPCs incorporating ZrO$_2$ nanoparticles, which means a more than 30-fold reduction as compared with those of these NPCs incorporating TiO$_2$ nanoparticles and is lower than that (≈12 cm$^{-1}$) of the sol–gel photopolymer with MA:Zr complex species. This means that the transmittance of a ZrO$_2$ dispersed NPC film of 500 $\mu$m thickness (the minimum thickness for HDS media (27)) is approximately 92%, useful for many holographic applications including HDS. Later, volume holographic recording in acrylate-based NPCs incorporating ZrO$_2$ nanoparticles at UV (364 nm) (38, 49) and violet-blue (404 nm) (51) wavelengths was reported. It was found that the optimum concentration of ZrO$_2$ nanoparticles at 404 nm was the same as that at 532 nm as seen in Figure 9.

3.1.1.4. SiO$_2$ nanoparticle dispersion. Low refractive index nanoparticles, together with high refractive index polymer, can also be used to increase $\Delta n_{sat}$. Indeed, Suzuki and Tomita (40, 41) reported NPCs incorporating SiO$_2$ nanoparticles having the bulk refractive index of 1.46. Note that a practical advantage of using SiO$_2$ nanoparticles is the ease-to-prepare in small (∼10 nm or smaller) size as well as in their spherical shape. In their work, SiO$_2$ nanoparticles (13 and 36 nm in diameter) were dispersed in a solution of methyl isobutyl ketone. This SiO$_2$ nanoparticle sol was then added to high refractive index methacrylate monomer, 2-methyl-acrylic acid 2-[4-[2-(2-methyl-acryloyloxy)-ethylsulanylmethyl]-benzylsulfanyl]-ethyl ester (124), whose refractive index was 1.59 after polymerization. Titanocene photoinitiator was also added in 1 wt% with respect to the monomer, providing the photosensitivity in the green. Note that the recording sensitivity can be increased by approximately 10 times in the green by adding appropriate sensitizing dyes (39). It was found that the optimum concentration of SiO$_2$ nanoparticles (13 nm) was 34 vol.% at which $\Delta n_{sat}$ gave the largest value of $8 \times 10^{-3}$ at grating spacing of 2 $\mu$m (see Figure 8). It was shown that while $\sigma$ was reduced down to 2.7% by the dispersion of 40 vol.% SiO$_2$ nanoparticles, thermo-optic coefficients and linear coefficients of thermal expansion (CTE) could also be reduced significantly by the dispersion of SiO$_2$ and ZrO$_2$ nanoparticles (see Figure 10) (70). Furthermore, it was found that while scattering loss was as low as 2% for a 45 $\mu$m-thick NPC film with SiO$_2$ nanoparticles of 13 nm, it increased significantly with an increase in nanoparticle size from 13 to 36 nm and thereby $\Delta n_{sat}$ decreased with an increase of film thickness when the scattering loss was significant (41). Thanks to high-quality NPC volume gratings with 13 nm SiO$_2$ nanoparticles, the overmodulation effect (the optical Pendellösung interference effect (24, 153)) could be observed for a 90 $\mu$m NPC film incorporating 34 vol.% SiO$_2$ nanoparticles (41). Taking advantage of such a high-quality thick NPC grating and a relatively
large coherent scattering length density of SiO₂ for slow neutrons, Fally et al. successfully demonstrated for the first time slow-neutron diffraction with NPC gratings with SiO₂ nanoparticles (84), which will be described in Section 4.2. Later, volume holographic recording in SiO₂ nanoparticles dispersed to either binder matrices or azopolymer was investigated (42, 43, 45, 46, 48, 53).

### 3.1.1.5. Semiconductor nanoparticle (quantum dot) dispersion

QDs that confine optically excited electron–hole pairs in all three space dimensions are of considerable interest in science and engineering (154). Their potential applications in photonics include QD lasers/LEDs, photovoltaic solar cells, fluorescent biological tags for deep tissue imaging, nonlinear optics, and quantum information science. They can be fabricated by various techniques such as electron-beam lithography, self-organized growth by the Stranski–Krastanow transition, growing semiconductor microcrystallites in glass matrices, and colloidal synthesis in liquid. Furthermore, tailored patterning of QDs dispersed in a thick polymer matrix is of great interest for photonic and biomedical applications. So far, QD patterning by direct printing, layer-by-layer, and shadow-mask lithographic techniques was demonstrated (7, 155). Because of the quantum confinement effect in a QD (156) and the electromagnetic feedback in Bragg grating structures, it is expected that QD-dispersed NPCs with Bragg grating structures constructed by holographic assembly of QDs enhance optical nonlinearity (157).

Liu et al. (62) demonstrated holographic assembly of CdSe QDs in a blend of ionic liquid and acrylate monomers to fabricate volume Bragg grating structures with diffraction efficiency near 100%. This single-step holographic method does not require a shadow mask and can fabricate centimeter size multidimensional photonic lattice structures. They employed an aqueous synthesis of surface-treated CdSe QDs (3 nm in diameter) whose quantum-confined electron–hole transition was peaked at ∼470 nm, followed by extraction of QDs into the ionic liquid monomer for the uniform dispersion of CdSe QDs in the monomer blend. Titanocene photoinitiator was also added in 1 wt% with respect to the monomer, providing the photosensitivity in the green. An aliphatic urethane hexacrylate monomer was added to the polymerizable ionic liquid monomer doped with CdSe QDs and the titanocene, enabling high cross-linking networks during polymerization to facilitate holographic assembly of CdSe QDs under holographic exposure. It was shown that fabricated 45 μm-thick transmission volume grating with 0.34 vol.% (1.3 wt%) CdSe QDs gave the diffraction efficiency near 100% and ∆n_sat as high as 5.1 × 10⁻³ at a recording and readout wavelength of 532 nm. Further dispersion of CdSe QDs up to 6.8 vol.% (27 wt%) resulted in ∆n_sat as large as 1.8 × 10⁻² at the optimum concentration of the acrylate co-monomer (see Figure 11) (158). It was also shown that the CdSe QD-dispersed NPC film exhibited negative third- and positive fifth-order nonlinear refraction, together with the saturable absorption behavior, in response to a 532 nm picosecond laser pulse (81, 158). Nonlinear behavior of the diffraction efficiency of an NPC volume grating was also observed in an NPC incorporating TiO₂ nanoparticles (159). Sakho et al. (53) demonstrated holographic recording at 365 nm in NPCs incorporating various types of semiconductor QDs such as CdS, ZnS, CdSe, CdZnS₂, and CdSe/ZnS. Although commercially available, CdSe/ZnS QDs (4 nm in diameter) show the highest quantum yield of photoluminescence among these QDs and could be dispersed only below 3 wt%. On the other hand, CdZnS₂ (4–7 nm in diameter) having a moderate quantum yield was able to be dispersed at the concentration of 20 wt% with appropriate reagents. Barichard et al. (63, 64) also investigated the photopolymerization process and volume holographic recording at 488 nm in NPCs incorporating CdSe/ZnS QDs (5.2 nm in diameter). It was found that the presence of QDs gave a noticeable decrease in the polymerization rate due to the trap of a co-initiator at the surface of QDs, facilitating the diffusion of monomer and QDs under inhomogeneous light illumination and thereby increasing ∆n_sat to as large as 6.8 × 10⁻³ at 0.5 wt% CdSe/ZnS QDs.

Since these semiconductor QDs and other luminescent nanoparticles such as LaPO₄ : Ce³⁺, Tb³⁺ exhibit efficient photoluminescence, NPC gratings incorporating QDs may be used for DFB laser structure with its emission-tuning capability. Smirnova et al. (160) demonstrated for the first time amplified spontaneous emission at ∼575 nm from an NPC Bragg grating co-incorporating CdSe/ZnS QDs and ZrO₂ nanoparticles, where CdSe/ZnS
QDs (ZrO$_2$ nanoparticles) were used for a gain (Bragg) grating. They also showed lasing action at 562–606 and 568–625 nm from NPC Bragg gratings incorporating ZrO$_2$ (161) and LaPO$_4$:Ce$^{3+}$, Tb$^{3+}$ (162) nanoparticles, respectively, which were co-doped with Pyromethen 567 laser dye. Peak pump/output conversion efficiencies of $\sim$3 and $\sim$8%, respectively.

**3.1.2. Use of free radical-mediated step growth polymerization**

So far, we have shown that the incorporation of nanoparticles in MA photopolymer capable of free radical-mediated chain growth photopolymerizations gave an increase in $\Delta n_{\text{sat}}$, exceeding the required minimum value of $5 \times 10^{-3}$ for large storage capacity of HDS media (27). It also led to a substantive reduction in polymerization shrinkage and improved thermal stability. However, polymerization shrinkage of the order of 1% for recorded NPC gratings was still larger than the required criterion of 0.5% that needs to be met to avoid the hologram distortion that severely reduces the readout fidelity of recorded information (27). Such large shrinkage happens because the van der Waals distance between monomer molecules before polymerization is converted to the covalent bond distance upon polymerization so that the resulting polymerization-induced microscopic free volume loss exhibits 22.5 ml shrinkage/mol C = C polymerized for chain growth MA photopolymers and causes macroscopic volume shrinkage (163, 164). To further mitigate polymerization shrinkage occurring in NPC films during recording, Hata et al. (73–75), and Mitsube et al. (76) proposed the use of TE and TY photopolymerizations that proceed via a step growth radical addition mechanism for volume holographic recording in NPCs. Using such a new NPC system, Momose et al. demonstrated holographic shift multiplexing of more than one hundred 2D digital data pages with high fidelity readout (78, 79). This demonstration will be described in Section 4.1.

Figure 12(a) illustrates TE systems (165) that use the step growth polymerization. It proceeds by a step growth radical addition mechanism via sequential propagation of a thiol radical (RS) through a vinyl (an ene) monomer (R$_1$CH=CH$_2$) and the subsequent chain transfer of a generated thioether radical (R$_1$C-H = CH$_2$-SR) to a thiol (RSH), regenerating a thiol radical and forming a thioether (R$_1$CH$_2$-CH$_2$-SR). Shrinkage occurring before the gelation can be readily accommodated by the liquid mixture of oligomers (163); the TE photopolymerizations proceed very rapidly but will not reach the gel point until high functional group conversions, resulting in 12–15 ml shrinkage/mol C=C polymerized (164), which represents notable reductions in shrinkage and stress when compared to that for MA systems as mentioned above. Other advantages of TE polymerizations include low toxicity and the absence of oxygen inhibition.

However, the TE polymerizations typically result in, as compared to MA photopolymers, low cross-linking densities and thereby low glass transition temperatures, leading to the limited thermal stability of a recorded grating. This is so because the conversion of a vinyl to a thioether provides the vinyl group as monofunctional in TE photopolymerizations. The thermal stability may be improved by use of radical-mediated TY step growth photopolymerizations (166) with keeping the low shrinkage ability of the TE photopolymerizations, as shown in Figure 12(b). It is different from the TE photopolymerizations in such a way that each alkyne functional group can react consecutively with two thiol functional groups. A thiol radical adds across the alkyne ‘triple bond’ (R$_1$C≡CH), forming a vinyl sulfide radical (R$_1$CH=CH-SR). This radical abstracts a hydrogen atom from a thiol, regenerating a thiol radical and forming a vinyl sulfide (R$_1$CH=CH-SR). Then, a thiol radical adds across the ‘double bond’ of the vinyl sulfide, generating a dithioether radical. This process is followed by the abstraction of a hydrogen atom from a thiol by the dithioether radical, regenerating a thiol radical and forming a dithioether.

Hata et al. (73–75) demonstrated one order-of-magnitude reduction of shrinkage with TE-based NPCs incorporating SiO$_2$ nanoparticles. It was shown that the stoichiometric composition of multifunctional mercaptopropionate thiols and allyl ether enes incorporating 25 vol.% SiO$_2$ nanoparticles gave shrinkage reduction below 0.5% with $\Delta n_{\text{sat}}$ as large as $8 \times 10^{-3}$ and $S$ as high as 1014 cm/J at a recording and readout wavelength of 532 nm (73). The reduced shrinkage was the same order as other low-shrinkage dry photopolymer systems such as those including a high content of inert binder components and using monomers capable of cationic
ring-opening polymerization (CROP) \(167\). However, the thermal stability of recorded holograms was not high enough due to the use of organic HBP nanoparticles. Soon later, they showed improved thermal stability using a new TE combination of secondary dithiol and allyl triazine triene (TATO) together with SiO\(_2\) nanoparticles \(74, 75\). This TE-based NPC system gave \(\Delta n_{\text{sat}}\) as large as \(1 \times 10^{-2}\), \(S\) as high as 1615 cm/J and \(\sigma\) as low as 0.4%, satisfying the acceptable condition of \(\Delta n_{\text{sat}} \geq 0.005, S \geq 500\) cm/J and \(\sigma < 0.5\%\) for HDS media \(27\). Later, volume holographic recording in TE-based NPCs incorporating SiO\(_2\) nanoparticles at a violet-blue wavelength (404 nm) was also reported \(77\).

Mitsube et al. \(76\) employed the stoichiometric composition of a TY monomer blend consisting of trithiol monomer, trimethylolpropane tris(3-mercaptopropionate), and diyne monomer, 1, 7-octadiyne, together with a co-monomer, N-vinyl-2-pyrrolidone (NVP), as a plasticizer to disperse SiO\(_2\) nanoparticles. They showed that the TY-based NPC incorporating 20 vol.% SiO\(_2\) nanoparticles gave \(\Delta n_{\text{sat}}\) as large as 0.008 and \(S\) as high as 2220 cm/J at a recording and readout wavelength of 532 nm. They also showed that although \(\sigma\) could be reduced only to 1.0% due to the addition of NVP, the thermal stability was improved better than that of the TE-based NPC system when SiO\(_2\) nanoparticles are used.

Figure 13 shows dependences of SiO\(_2\) nanoparticle concentrations on \(\sigma\) [Figure 13(a)] and CTE \(\alpha_L\) [Figure 13(b)] for NPC plane-wave volume gratings using TE, TY, and MA monomers. In these measurements, Dhar et al.’s holographic method \(152\) was used to estimate their values for \(\sigma\) and \(\alpha_L\). The detailed method is described in \(70\). It can be seen that both \(\sigma\) and \(\alpha_L\) decrease with increasing concentrations of SiO\(_2\) nanoparticles for all NPCs. Although values of \(\sigma\) for both TE and TY are much smaller than that of MA, that of TY is larger than that of TE due, presumably, to the addition of NVP in TY. On the other hand, values of \(\alpha_L\) for TE and TY are larger than that for MA due to the fact that MA has highly cross-linking structures after curing. Nevertheless, the decreasing rate of \(\alpha_L\) for TY tends to be larger than that for TE with increasing the concentration of SiO\(_2\) nanoparticles due to the TY reaction shown in Figure 12(b).

### 3.2. Organic NPC systems

#### 3.2.1. Use of free radical-mediated chain polymerization

For the preparation of NPCs with good optical quality, it is required that nanoparticles be uniformly dispersed without unwanted aggregation and chemical reaction with other components. Therefore, appropriate surface treatment is always necessary for inorganic nanoparticles to disperse them uniformly. To relax this somewhat severe requirement, nanostructured polymers that possess highly branched main chains such as dendrimers \(168\) and HBPs \(169\) can be considered for size and refractive index controllable organic nanoparticles. Among them, HBPs are preferable from a viewpoint of the ease of preparation as well as of the uniform dispersion in host monomer without any substantive aggregation and unwanted chemical reaction/geometrical entanglement with monomer molecules, so that samples with good optical quality are easily available. They would behave themselves like well-shaped nanoparticles (i.e. hard nano-spheres). Moreover, unlike inorganic nanoparticles such as SiO\(_2\) nanoparticles that exhibit slight acidity, organic HBP nanoparticles can also be dispersed in monomer capable of CROP. It is also possible to control the optical properties of an HBP molecule and to add other photonic functionalities (e.g. photochromism and optical nonlinearity) by means of chemical treatment of functional end groups.
Figure 13. Dependences of (a) $\sigma$ and (b) $\alpha_L$ on SiO$_2$ nanoparticle concentrations for recorded NPC plane-wave volume gratings using TE, TY, and MA monomers, where 1 \mu m grating spacing was used for each NPC at a recording wavelength of 532 nm. Solid lines are a guide to the eye. (The colour version of this figure is included in the online version of the journal.)

Figure 14. Molecular structures of hyperbranched polymers: (a) HPEMA and (b) HPS.

Tomita et al. (65, 170) demonstrated volume holographic recording in NPCs incorporating HBPs acting as organic nanoparticles. They prepared the following two types of HBPs of approximately 10 nm size (estimated by an AFM): hyperbranched poly(ethyl methacrylate) (HPEMA) and hyperbranched polystyrene (HPS), as illustrated in Figure 14(a) and (b), respectively. Their heterogeneity indices, defined as $M_w/M_n$ (where $M_w$ and $M_n$ are the weight-average molar mass and the number-average molar mass, respectively) that indicate the relative size distribution of polymers, were estimated to be 1.68 and 4.86 for HPEMA and HPS, respectively. They are categorized into the AB*-type HBPs in which a seed inimer possesses both a polymerizable functional group A and an initiation functional group B. Inimers react one another under UV light illumination, leaving the group B behind to form an HBP structure of approximately spherical shape. Hydrogen termination (the reduction treatment) on the dithiocarbamate end group around the periphery of both HPEMA and HPS was performed with tributyltin hydride by radical transfer, making it unreactive in cross-linking chemistry during photopolymerization. After the reduction treatment, HPEMA and HPS had refractive indices of 1.51 and 1.61, respectively, at a wavelength of 589 nm.

In their holographic recording experiment, high refractive index methacrylate monomer, 2-methyl-acrylic acid 2-[4-\{2-(2-methyl-acryloyloxy)-ethylsulfanyl\}ethyl ester, used for SiO$_2$ nanoparticle-dispersed NPCs (41), and low refractive index methacrylate monomer, 2-methyl-acrylic acid 3-(2-methyl-acryloyloxymethyl)-octahydro-4,7-methanoinden-5-ylmethyl ester, used for TiO$_2$ nanoparticle-dispersed NPCs (35), were employed for HPEMA and HPS organic nanoparticles, respectively, to obtain a large difference in refractive index between monomer and nanoparticles. Each HBP was initially dissolved in tetrahydrofuran and was mixed to the corresponding monomer and 1 wt% titanocene photoinitiator. Figure 15 shows a dependence of $\Delta n_{sat}$ on concentrations of HPEMA and HPS organic nanoparticles. It can be seen that, as similar to inorganic nanoparticle-dispersed NPCs, an optimum concentration maximizing $\Delta n_{sat}$ exists. Such concentration-dependent behavior of $\Delta n_{sat}$ is qualitatively in agreement with the prediction by several phenomenological models (98, 100, 104, 105). The maximum value of $\Delta n_{sat}$ for HPEMA nanoparticle-dispersed NPCs is more or less comparable to those for inorganic ZrO$_2$ and SiO$_2$ nanoparticle-dispersed NPCs at a recording wavelength of 532 nm. It was found that $\sigma$ could be reduced to 2.3 and 3.0 % for NPCs incorporating 40 vol.% HPEMA and HPS organic nanoparticles, respectively. Periodic assembly of HBP organic nanoparticles in the formed polymer was also examined under holographic exposure, as shown in Figure 2(b). These results indicate that HBP organic nanoparticles play the same role as inorganic
nanoparticles in the holographic grating formation. Recently, Tomita et al. reported $\Delta n_{\text{sat}}$ as large as $2.2 \times 10^{-2}$ at 532 nm for a new NPC incorporating HBP organic nanoparticles having ultrahigh index of refraction of 1.82 (171).

### 3.2.2. Use of CROP

CROP provides lower polymerization shrinkage than chain polymerization due to the ring-opening mechanism during photopolymerization (172). Waldman et al. (167) showed that all-organic photopolymer incorporating CROP monomer and inert binder polymer gave $\Delta n_{\text{sat}}$ larger than $7 \times 10^{-3}$ and polymerization shrinkage of the order of 0.1%. Since HBP organic nanoparticles are generally easy to disperse in many types of monomers, there is an opportunity to achieve low shrinkage with CROP monomer-based NPCs incorporating HBP organic nanoparticles. Indeed, Tomita et al. (170) investigated the holographic recording properties of CROP monomer-based NPCs incorporating HBP organic nanoparticles. They used a CROP monomer system of oxetane monomer, 1,4-bis[(3-ethyl-3-oxetanyl)methoxy]benzene, and epoxy monomer, 7-oxabicyclo(1,4)heptan-3-yl-methyl-7-oxabicyclo(1,4)heptane-3-carboxylate. HPS organic nanoparticles without the reduction treatment were employed since they had the refractive index of 1.69, higher than that of HPS (= 1.61) with reduction treatment and thus they gave a larger refractive index difference from that of the polymer blend (= 1.54) than HPEMA organic nanoparticles. Iodonium salt (5 wt%) was used as a cationic photoinitiator together with titanocene (25 wt%) as a visible photosensitizer for holographic recording at 532 nm.

Figure 16 shows the recording dynamics of $\Delta n_{\text{sat}}$ for different concentrations of HPS nanoparticles at grating spacing of 1.5 µm.

4. **Holographic applications**

In this section, we describe two examples of holographic applications of using photopolymerizable NPCs. These include HDS and neutron optics. These applications are very different from each other in a fundamental sense that while the former uses the electromagnetic interaction between light and matters, the latter relies on the neutron–nuclear interaction in matters. It is shown that holographic NPC gratings can give good performance in these applications utilizing completely different interactions. For other interesting applications, security and sensors readers are encouraged to consult Refs. (52, 80) for their detailed information.

### 4.1. Holographic data storage

4.1.1. **Photopolymerizable NPCs as HDS media**

HDS systems have been extensively studied for more than four decades owing to an ever-increasing demand
for more efficient and much denser information handling capabilities in our present and future information societies. Current trends in developing practical HDS systems stem from the fact that cost-effective devices such as laser diodes, spatial light modulators (SLMs), and CCD/CMOS have been available for peripheral system components. Among various holographic recording materials considered for HDS applications, such as photorefractive (173), photo-addressable (174), photopolymer (175), and photochromic (176) materials, only photopolymers have been currently considered to be commercially viable materials for HDS media in write-once read-many HDS systems due to both performance and the costs (177). Requirements for practical HDS media generally include $\Delta n_{\text{sat}} \geq 5 \times 10^{-3}$ (or $M/\# \geq 10$) for large storage capacity, $S \geq 500 \text{ mJ/cm}$ for high recording speed at limited recording power, $\sigma < 0.5\%$ and high thermal stability for high readout fidelity, and high environmental stability (27, 177). As described in Section 3.1.2, volume gratings recorded in the TE-based NPC incorporating inorganic SiO2 nanoparticles satisfy these requirements (73, 74), suggesting their use for HDS media. Indeed, it was shown that TE-based NPCs gave good performance in shift-multiplexed holographic digital data page storage (78, 79).

4.1.2. Experiments and results

Figure 17 shows a two-beam recording setup for shift-multiplexed holographic recording (179). The linearly polarized laser beam from a frequency-doubled diode-pumped Nd:YVO4 laser operating at 532 nm was used as a coherent light source. After the beam expansion and collimation, it was divided into two beams, one for a reference and the other for a signal, by the half mirror. A spherical reference beam loosely focused by a lens was used. The signal beam passed through a computer-controlled electric shutter and was normally incident on a transmission-type liquid crystal SLM with 800×600 pixels and a pixel pitch of 32 $\mu$m, which was sandwiched between two polarizers to obtain a high-contrast digital data page input (180). This way, two-dimensional digital data page information was encoded on the signal beam and the transmitted signal beam was Fourier transformed by a tandem combination of a 4f lens system and another lens. A TE-based NPC described in Section 3.1.2 was used as a recording film sample of $\sim 250$ $\mu$m thickness. It employed a stoichiometric blend of dithiol and triene (TATATO) monomers that were incorporating 25 vol.% SiO2 nanoparticles. The reconstructed two-dimensional data page was imaged onto a 1600 $\times$ 1200 CCD camera with 4.4 $\mu$m pixels at a magnification of $\times0.25$ and an oversampling rate of 4. When the diffraction efficiency from each recorded data page hologram was measured, the CCD camera was replaced by a Si detector.

Various symbol modulation coding formats were used to encode two-dimensional digital data page information with randomly generated balanced-binary data bits (i.e. an equal number of 0 and 1s), as shown in Figure 18. These include a one-dimensional 1:2 modulation code expressing 1 bit of data using one pair of bright (unity transmissivity) and dark (zero transmissivity) bits and also two-dimensional 2:4, 5:9, 9:16, 10:16, and 13:25 modulation codes (181). The symbol modulation coding can mitigate decoding errors that would take place due to intensity irregularities of symbol modulation code patterns in a reconstructed data page. This is possible by means of the so-called differential bit classification (181) that determines bright code block portions by comparing all bright and dark code blocks within a $\sqrt{n} \times \sqrt{n}$ code block. In this shift-multiplexed recording experiment, 10 different digital data pages with each symbol modulation coding were numerically generated and were sequentially

![Figure 17. Two-beam recording setup for shift-multiplexed HDS. (The colour version of this figure is included in the online version of the journal.)](image-url)
used as input data pages. After recording one-volume hologram, a transversal shift of 180 µm was made to record the next hologram, which was determined from the third null distance in a shift–distance dependence of the diffraction efficiency of a recorded volume hologram for a data page with all pixels on (i.e. unity transmissivity). This shift per hologram upon multiplexing corresponds to 11 holograms partially overlapped on another within the signal beam’s spot. The detailed shift-multiplexing procedure, together with pre-exposure method, was described in (78).

Figure 19 shows typical examples of input and reconstructed images of digital data pages coded with 2:4 and 9:16 symbol modulation coding formats as shown in Figure 18. These sample images are taken from the 21st data page hologram in recording order. It can be seen that these input images are reconstructed with high fidelity. It is known that error-free retrieval of data pages with a raw bit-error rate (BER) lower than 4 × 10^{-3} or a symbol error rate (SER) lower than 1 × 10^{-1} is possible with an error-correction code (ECC) (182). Therefore, the baseline performance of the optical system was sufficient to evaluate the holographic data page recording capability of the TE-based NPC. It was found that shift-multiplexed 250 holograms gave more or less uniform diffraction efficiencies of the order of 1 × 10^{-4} without specific scheduled recording.

SERs and signal-to-noise ratios (SNRs) of reconstructed 250 holograms as a function of data page number for various symbol modulation coding formats are shown in Figures 20 and 21, respectively. It can be seen that all SERs are lower than 1 × 10^{-1}, implying that error-free retrieval of data pages is possible with ECC. All measured SNRs are larger than 2. It is noted that higher modulation coding generally provides lower SERs and higher SNRs.

A parametric plot of SNRs and SERs for different symbol modulation coding formats is shown in Figure 22, where error bars span the minimum and maximum values for SERs and SNRs among all 250 reconstructed images. It can be seen that the 5:9, 9:16, and 13:25 modulation codes give lower SERs with higher SNRs among others. These modulation codes possess low white rates among others, giving rise to a reduction in low spatial frequency components relative to high frequency ones in their digital data page patterns. Such a DC-reduced spatial frequency distribution provides high-contrast refractive index modulation in an NPC film, so that low SERs and high SNRs can be obtained (183). It can also be seen that the readout fidelity (i.e. an SER and an SNR) for the 9:16 (13:25) modulation code is much better than that for the 10:16 (15:25) modulation code having the same 4 × 4 (5 × 5) code block. This is so because a 1 (bright) bit error leads to higher SER in a modulation code having larger bits of data.

Considering the coding efficiencies, it is found that the 9:16 modulation code is the highest among the 5:9, 9:16, and 13:25 modulation codes. This result is similar to Kume et al.’s work (181), showing that the use of the 9:16 modulation code rather than other lower and higher modulation codes improves an SER and an SNR better in angularly multiplexed holographic digital data storage using a photorefractive strontium barium niobate crystal. The linear areal data density for the 9:16 modulation code is calculated to be $900 \times 9 \times 11/(\pi \times 1^2) = 28362\text{ bit/mm}^2 \approx 19\text{ Mbit/in.}^2$. The average diffraction efficiency for the 9:16 modulation code is of the order of 10^{-4}. Note that the $1 \times 10^{-5}$ is the minimum diffraction
Figure 20. SERs of reconstructed holograms as a function of data page number for 1:2, 2:4, and 5:9 symbol modulation coding formats (above) and for 9:16, 10:16, and 13:25 symbol modulation coding formats (below) (79). The horizontal dotted lines are a guide to the eye. (The colour version of this figure is included in the online version of the journal.)

Figure 21. SNRs of reconstructed holograms as a function of data page number for 1:2, 2:4, and 5:9 symbol modulation coding formats (above) and for 9:16, 10:16, and 13:25 symbol modulation coding formats (below) (79). The horizontal dotted lines are a guide to the eye. (The colour version of this figure is included in the online version of the journal.)
efficiency for Gbit/s readout with reasonable laser power (184).

Figure 23(a) shows an input of one digital data page coded with 9:16 symbol modulation coding format for coaxial holographic digital data recording (182, 185) that employed a single 532 nm laser beam and an objective lens (NA0.80). The corresponding reconstructed images from holograms recorded in TE and TY NPCs are shown in Figure 23(b) and (c), respectively. It was found that BERs, SERs, and SNRs were $2 \times 10^{-3}$ ($3 \times 10^{-3}$), $< 1 \times 10^{-4}$ ($< 1 \times 10^{-4}$), and 6 (7), respectively, for a hologram recorded in TE (TY) NPCs. This result indicates that TE and TY NPCs show good performance as HDS media.

4.2. Neutron optics

4.2.1. Diffraction gratings and multilayer structures for neutron optics

Neutron optics, neutron diffraction, and neutron scattering methods are important for fundamental physics (186–189) as well as condensed matter physics (190, 191). Considering the number of operated neutron research centers and efforts put into those facilities (192) in Europe alone (e.g. the construction of the European Spallation Source in Lund, Sweden), the advancement of novel neutron optical techniques is necessary. For example, devices deployed nowadays to produce a polarized beam of cold neutrons (CN), i.e. a long-wavelength neutron beam prepared in a well-defined spin state, are bulky and rather expensive. There is clear lack of versatile, compact, and low-cost alternatives similar to those available in light optics. To spark such development, NPC gratings have been introduced as neutron optical elements for cold and very cold neutrons (VSN) (i.e. slow neutrons) (84–87).

The one-particle Schrödinger equation lies at the heart of the theoretical basis of neutron optics (see, e.g. (193)). It contains the neutron optical potential ($V_N$) describing the interaction of neutrons with the nuclei in a nonmagnetic material. The neutron refractive index of the material ($n_{neu}$) is given by $\sqrt{1 - \frac{V_N}{E_0}} \approx 1 - \lambda_{neu}^2 \frac{b,\rho}{(2\pi)}$ at a certain de Broglie wavelength ($\lambda_{neu}$). Here, $b,\rho$ is the coherent scattering length for a particular isotope, which is proportional to the scattering cross section, $\rho$ is the atomic number density, and $E_0$ is the energy of the incident free neutrons. The collective quantity $b,\rho$ is usually called the scattering length density of a mono-isotopic material. A sinusoidal grating, say, a piece of material periodically patterned in the $x$-direction, can thus be characterized by the neutron refractive index function

\[ n_{neu}(x) = n_{neu} + \Delta n_{neu} \cos \left( \frac{2\pi x}{\Lambda} \right), \]

where $\Delta n_{neu}$ is the modulation amplitude of $n_{neu}$ given by $\lambda_{neu}^2 b,\rho / (2\pi)$, in which $\Delta \rho$ is the number density modulation amplitude, and $\Lambda$ is the grating spacing as defined in Equation (5). Note that a tentative phase shift $\Phi$ appeared in Equation (5) is not incl in Equation (13) as it does not play any role when it comes to the diffraction properties. In the above description, coherent interactions with magnetic materials embedded in a nonmagnetic matrix can be introduced by adding a spin and magnetic field-dependent part ($\pm \rho(B)$) to $n_{neu}$, with the magnetic flux density ($B$). We obtain $\Delta n_{neu} \pm = \lambda_{neu}^2 [b,\rho \pm \lambda_{m}] / (2\pi)$, where the subscripts $m$ indicates the respective quantities for the magnetic material component. The magnetic contribution to the neutron scattering amplitude might be of the same order of magnitude as the nuclear contribution (194, 195). Similarly, for the description of neutron interactions with absorbing materials embedded in a matrix, an imaginary term can be added and $b,\rho \Delta \rho$ is replaced by $b,\rho - (b,\rho \Delta \rho - (b,\rho \Delta \rho) \lambda_{m}$, where the subscript $a$ denotes the respective quantities for the absorbing material component.

Widely used ‘grating structures’ in thermal neutron optics (for $\lambda_{neu}$ around 1.9 Å) are mostly crystal lattices. They have been used as monochromators, wavelength analyzers, polarizers, and beam splitters for neutron interferometry to name but a few. Due to their rather small lattice constants, most crystals cannot be used for slow-neutron optics with CN at 4 Å < $\lambda_{neu}$ < 30 Å (190) and with VCN at 30 Å < $\lambda_{neu}$ < 100 Å, simply because the Bragg condition $\lambda_{neu} = 2\Lambda \sin \theta_B$ cannot be fulfilled at $\lambda_{neu} > 2\Lambda$. For CN and VCN interferometry, artificial structures have been adopted successfully: Ni gratings in reflection geometry in combination with mirrors (196), or quartz glass transmission gratings at a period of about 2 µm (197), have been applied. Furthermore, multilayer mirrors have also been employed (198). Phase and absorption gratings fabricated by photolithographic tech-
4.2.2. Neutron diffraction experiments with holographic gratings

Several material classes have been considered as candidates for holographic production of diffractive elements for neutron optics (142). Investigations of deuterated (poly)methylmethacrylate gratings (202) led to successful demonstration of neutron interferometers for CN at Institut Laue–Langevin (ILL, Grenoble, France) by Schellhorn et al. (203) and Pruner et al. (204). Those interferometers operate in just the same manner as perfect crystal Si neutron interferometers (186). Also, HPDLCs led to promising results for diffraction-based neutron optical components (205). As described in Section 3, a great advantage of holographic NPC gratings is the versatility of NPC materials due to the wide range of possible choices among various synthetic nanoparticles. One can select the most suitable value of $\Delta n_{\text{neu}}$ for a specific application. For example, the magnetic and absorptive terms shown in Section 4.2.1 may be added to the periodic optical potential by incorporating ferromagnetic/superparamagnetic nanoparticles and Gd or CdSe nanoparticles, respectively. Magnetic grating structures can also be used as polarizing beam splitters for retrofitting small-angle neutron scattering (SANS) instruments. Absorption gratings with small $\Lambda$ could find applications in VCN interferometry.

In comparison with light optical experiments using NPC gratings discussed in the previous sections, a couple of peculiarities occur in related neutron diffraction experiments. Since NPC gratings usually have periodicities that are much larger than the wavelength of incident neutrons, $\theta_B$ given by $\arcsin(\lambda_{\text{neu}}/2\Lambda)$ is of the order of 0.1°, which is within the regime of SANS. A typical neutron diffraction experiment with an NPC grating is sketched in Figure 24 (left). In this example, a SiO$_2$ nanoparticle-dispersed NPC grating (41) (with a nanoparticle concentration of 25 vol.%, $\Lambda = 0.5 \mu$m and the film thickness $\approx 100 \mu$m) is mounted in transmission geometry (also called the Laue-geometry) and is tilted through the angle ($\zeta$) around an axis parallel to the grating vector pointing in $x$-direction. The tilt is made to increase the effective thickness ($d$) of the NPC grating, if necessary, which will be described in Section 4.2.3. The incident angle ($\theta$) is varied to measure the diffraction efficiency ($\eta$) as a function of $\theta$ (the so-called ‘rocking curve’), see Figure 24 (right) in the vicinity of $\theta_B$.

The beam diameter may vary from fractions of millimeters to several centimeters, depending on the sample
size as well as neutron flux and available beam time. The spatial resolution of SANS detectors, mostly 2D detectors, is typically in the range of several millimeters. Due to the large collimation distance available (up to 20 m) and the finite spectral width of an incident CN beam, this enables to resolve structures of target samples ranging from nanometers to a few microns in SANS measurements. The width of the wavelength distribution of an incident CN beam from a velocity selector is typically around 10% (see, e.g. Ref. (190)). The divergence angle of an incident CN beam, determined approximately by \((w_1 + w_2)/L\) \((w_1, w_2,\) and \(L\) are the diameters of two collimation apertures and the distance between them, respectively), is always chosen to be smaller than the expected angular width of a rocking curve (i.e. the angular distance between the two minima next to the Bragg angle position in the rocking curve). Note that the angular width of the rocking curve for most NPC gratings is approximately given by \(2\Delta \theta/d\), where \(d\) is given by \(d_0/cos\zeta\) (\(d_0\) is the physical film thickness of the NPC grating).

In SANS experiments with NPC gratings, the diffraction efficiency \(\eta_i\) for the \(i\)th diffraction order is defined as \(\eta_i(\theta) = I_i(\theta)/I_{tot}\), where \(I_i(\theta)\) and \(I_{tot}\) are the measured intensities of the \(i\)th diffraction spot and the total intensity of all diffraction spots on the detector, respectively. Then, \(\eta_i\) may be adjusted for a particular application by selecting experimentally controllable parameters such as \(b, \Delta \rho, \Lambda\), and the thickness \(d_0\), according to theories for a thick sinusoidal grating (e.g. Uchida’s theory (132), Kogelnik’s theory (131) and dynamical diffraction theory (186, 190, 191, 193)).

Depending on the above parameter values, more than two diffraction spots would appear at a certain \(\theta\). In this case, diffraction does not occur in Bragg regime (the two-wave coupling regime). Either the grating may be purely sinusoidal, but ‘optically thin’, rocking curves are therefore rather wide and may overlap as shown in Figure 25, or the grating may not be purely sinusoidal and further Fourier components are necessary to describe its refractive index modulation such that \(n_{neu}(x) = n_{neu} + \Delta n_{neu} \cos (2\pi x/\Lambda) + \Delta n_{neu} \cos (4\pi x/\Lambda) + \cdots\). In the latter case, the assumption of two-wave coupling could still be reasonable as long as the NPC grating is thick enough, so that the diffraction peaks in the rocking curve are narrow and well-separated on the \(\theta\)-axis. Terminology and details concerning these neutron diffraction phenomena are discussed in Section 2.4 and (141).

NPC gratings containing magnetic nanoparticles can also be used for obtaining polarized neutron beams in SANS measurements. The contrast between the diffraction efficiencies for two orthogonal incident neutron-spin states yields the information about \((\Delta n_{neu})_\pm\) from which \(p\) may be determined.

4.2.3. The Pendellösung interference effect
High diffraction efficiencies from thick holographic gratings recorded in photosensitive materials such as photographic silver halide emulsions, photorefractive materials, photopolymer, HPDLCs, and NPCs are sometimes inhibited by holographic scattering (207–211), especially in case their refractive index modulations are large. Such limitation of recordable material’s thickness for high diffraction efficiencies can be obviated by harnessing the so-called Pendellösung interference effect that occurs in diffraction from thick periodic structures. The physical mechanism of the effect is as follows: Upon entering a crystal or a holographic grating at the Bragg condition, the wave vector component of the neutron (or light) beam parallel to the surface must be conserved owing to the phase matching condition at the boundary. However, the wave vector component normal to the boundary is split in two, resulting in two standing waves inside the material: one in phase and the other out of phase with the periodic potential (i.e. the formed refractive index grating). The interference of these waves results in the energy exchange between diffracted and forward-diffracted (transmitted) beams along the thickness direction, depending on the crystal (grating) thickness (212), the incident wavelength (213), the angle of incidence, and the coherent scattering length density modulation amplitude (the refractive index modulation amplitude). The Pendellösung interference effect was predicted by dynamical diffraction theory (186, 193, 214, 215) and also by its fellow theories developed for visible light (131, 132, 193).
The Pendellösung effect for neutron diffraction by NPC gratings has been pointed out in Ref. (221) in which, based on Kogelnik’s theory, the expression for the oscillation of the first-order diffraction efficiency at the Bragg-peak ($\eta_p$) is given by

$$\eta_p = \sin^2 \left( \frac{\pi d}{\Delta} \right),$$

(14)

where the quantity $\Delta$ is usually called the Pendellösung period or the extinction length given by

$$\Delta = \frac{2\pi \cos \theta_B}{\lambda_{neu} \Delta \rho}$$

(15)

for NPC gratings. Here, $\Delta$ is in the range of 1 mm for NPC gratings at slow-neutron wavelengths. The Pendellösung effect can also be observed by tilting a crystal (or an NPC grating) around the axis parallel to the grating vector as $d$ appeared in Equation (14) increases (222). Consequently, in case increasing the recording thickness of an NPC grating is difficult due to holographic scattering, one may increase $d$ by tilting through the angle $\zeta$, as shown in Figure 24 (left) so that $\eta_p$ can be increased. Note that this could be done in the same way for light optic applications using NPC gratings.

4.2.4. Holographic slow-neutron optical elements using NPC gratings

4.2.4.1. NPC beam splitter for CN. Using the Pendellösung interference ‘trick’ explained above, one can readily turn NPC gratings with thickness-limited diffraction efficiencies into effective neutron optical elements by means of the grating’s tilt angle. The first example is the beam splitter behavior of an NPC grating of only about 102 $\mu$m thickness that directed the neutron beam of a SANS instrument with a quite broad wavelength spectrum ($\Delta \lambda_{neu}/\lambda_{neu} \approx 10\%$) into two different directions (84). Such a rocking curve is shown in Figure 26 (left). The data demonstrate splitting of an even wider VCN wavelength spectrum with $\Delta \lambda_{neu}/\lambda_{neu} \gtrsim 50\%$ (like the one in Figure 8(a) of Ref. (206)) by an NPC grating. The 50:50 beam splitting operation is clearly seen. Note that the grating diameter plays a crucial role when the grating is tilted. For example, an NPC grating’s diameter of 2 cm is shrunk to about 3.5 mm effective diameter (as seen by the neutron beam) at $\zeta = 80^{\circ}$.

4.2.4.2. NPC three-port beam splitter for CN. When examining different wavelengths and tilt angles for NPC gratings, one can realize many potentially useful configurations. For example, an NPC grating works as a three-port beam splitter at $\theta = 0^{\circ}$ as shown in Figure 26 (right). Such a device can be used for setting up a Zernike three-path interferometer for VCNs. Theoretically, the Zernike interferometer exhibits excellent phase sensitivity: the carpet-like intensity pattern formed in the plane spanned by the three paths is shifted by about 10 $\mu$m for a phase shift as small as $\lambda/100$ (87). A method of observing such carpet-like intensity patterns is proposed in Paragraph 4.2.5.4.

4.2.4.3. NPC mirror for VCN. One of the remaining limitations of holographic neutron optic elements based on NPCs is incoherent scattering and absorption in the NPC grating and its glass substrates. In order to avoid the latter problem, Klepp et al. employed a free-standing NPC grating (86). In their experiment, each one side of
the two glass substrates was coated with silane layers in order to remove the NPC grating (2 cm in diameter) from them after recording. This way, they could successfully obtain a free-standing NPC grating as shown in Figure 27 (left) and significantly reduce incoherent scattering and absorption, allowing them to go to large tilt angles of the free-standing NPC grating for an incident neutron beam of a couple of millimeters height. As a result, they demonstrated 90% diffraction efficiency (i.e. mirror-like behavior) as shown in Figure 27 (center, right) at λ_{neu} of about 41 Å with a free-standing NPC grating incorporating 20 vol% SiO₂ nanoparticles (Λ = 0.5 μm, d₀ ≈ 108 μm, ζ = 70°). Note that such a high diffraction efficiency was possible by achieving the required wavelength resolution with a time-of-flight system (190) by which one can resolve different neutron wavelengths according to their arrival times at the detector.

4.2.5.2. Diamond nanoparticle dispersion. Holographic NPC phase gratings incorporating diamond nanoparticles are promising as diamond has very high coherent and very low incoherent scattering cross sections for neutrons. At the same time, diamond exhibits low absorption. It is expected that diamond nanoparticle-dispersed NPC gratings with large values for b₀Δρ (i.e. large Δn_{neu}) could lead to the improvement of neutron mirrors and beam splitters, much the same way as already demonstrated previously (84–87), and to novel applications using the Pendellösung interference effect for fundamental physics.

4.2.5.3. Magnetic nanoparticle dispersion for polarizing beam splitter SANS add-on. The working principle of a grating-based polarizing beam splitter for neutrons is as follows: If an NPC grating incorporating magnetic nanoparticles is at the Bragg angle, diffracted and forward-diffracted (transmitted) beams are observable at the detector. As one increases, the external magnetic field applied to an NPC grating, the grating structure becomes invisible for neutrons in one spin state at certain values of the external magnetic field and ζ but acts as a mirror for neutrons in one spin state (224). That is, (Δn_{neu})_+ = λ^2_{neu}(b₀Δρ - [b_{c,m} + p(B)]Δρ_m)/2π becomes zero at B = B₀ while (Δn_{neu})_- = λ^2_{neu}(b₀Δρ - [b_{c,m} - p(B)]Δρ_m)/2π is equal to the value for mirror operation of the NPC grating at B = B₀. The saturation magnetic field of superparamagnetic nanoparticles, for example, can be well below 1 T, so that the external magnetic field could be provided by a quite small electromagnet even without cooling. The device (an electromagnet equipped with the NPC grating on a rotation stage, which may be a couple of centimeters in length along the beam direction) could be inserted just in front of the first collimation slit or pinhole, as an add-on to existing SANS setup. SANS signals from the
4.2.5.4. Absorption gratings. Neutron-absorbing materials such as Gd and CdSe could be used in their nanoparticle form to realize NPC absorption gratings (87). In this case, the diffraction by such an NPC absorption grating is of minor importance. Instead, it can be used as a shadow mask to detect the neutron interference fringe pattern by two or more mutually coherent neutron beams. As the NPC absorption grating moves step by step parallel to its grating vector, the interference pattern and its phase relative to the periodic structure of the NPC absorption grating can be estimated from the 'shadow image' of the NPC absorption grating at each grating position. This way, the intensity pattern formed in a Zernike three-path neutron interferometer could be observed. Also, Talbot–Lau 'carpet patterns' formed by self-imaging of an optically thin NPC grating could be observed and possibly exploited for fundamental physics investigations.

5. Summary

We have overviewed recent investigations of novel photopolymerizable nanocomposite photonic materials, the so-called photopolymerizable NPCs, and their holographic applications. Although the photopolymerization-driven diffusion phenomenon of photo-inactive organic molecular species (e.g. monomer and liquid crystal) in all-organic photopolymer has been known for 40 years, it is recently that, thanks to the development of nanotechnology, this phenomenon has been applied to assembling inorganic and organic nanoparticles in low viscous soft matter. We have discussed the mechanism of holographic grating formation in NPCs in terms of the photopolymerization-driven mutual diffusion model. The model considers the mutual diffusion of monomer and nanoparticles in NPCs under holographic exposure, where monomer molecules (nanoparticles) migrate to the bright (dark) regions of the light intensity interference fringe pattern. As a result, the density distributions of the formed polymer and nanoparticles are out of phase, inducing a holographic phase grating. Such a mechanism was confirmed experimentally by physicochemical and optical measurements for different types of NPC systems. We have also discussed the fundamental limit of $\Delta n_{\text{sat}}$ obtainable with NPCs. Since, in the limit of low nanoparticle concentrations, $\Delta n_{\text{sat}}$ is approximately proportional to a refractive index difference between the formed polymer and a nanoparticle and to a change in the volume fractions of dispersed nanoparticles in the dark and the bright regions, the refractive index of a nanoparticle needs to be either much lower or higher than that of monomer and to possess a large diffusion constant and good affinity with monomer. Although such requirements are fundamental for large $\Delta n_{\text{sat}}$, a more satisfactory statistical thermodynamics model that takes the size of a nanoparticle and the phase separation process into account is necessary to explain the grating buildup dynamics and perform the material optimization. We have also described several NPC systems reported so far. These consist of nanoparticles of metals, inorganic oxides, semiconductors, and organics dispersed in different types of photopolymer systems such as free radical-mediated chain/step growth and ring-opening polymerizations. We have explained pros and cons in their holographic recording properties in terms of $\Delta n_{\text{sat}}$, shrinkage, and thermal stability. These different NPC systems are designed and used for their suitable applications. Finally, we have briefly described two examples of our recent applications to holographic digital data storage and slow-neutron beam control. These successful demonstrations with high performance clearly show the usefulness of photopolymerizable nanocomposite photonic materials for versatile applications in photonics and other branches of physics such as neutron optics.

Further material improvement and new development of NPCs are expected. For example, the trade-off between shrinkage and thermal stability may be overcome to some extent by use of NPCs with monomer being capable of reversible addition-fragmentation Chain transfer polymerization (225) that provides low shrinkage and high cross-linking polymer networks at the same time. Also, the selection of nanoparticles would be naturally extended to other aspects rather than their refractive indices in light optics for qualitatively new applications. For example, NPC gratings incorporating diamond and magnetic nanoparticles would give better performance and new operations for neutrons as explained in Section 4.2.5 provided that a new fabrication technique allows us to prepare NPC gratings with these materials. Furthermore, all-optical and single-step capability of manipulating nanoparticle assembly in multi-dimensions and arbitrary orientations may be of significant importance in photonics, electronics, nanotechnology, synthetic materials research, and chemical/biomedical applications.

Acknowledgements

The authors would like to thank a number of key collaborators, including N. Suzuki, K. Furushima, K. Matsumura, J. Nozaki,
This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [grant number 15H03576].

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan [grant number 15H03576].

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