Temperature-Sensitive Holograms with Switchable Memory
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Herein, the dynamics and reversibility of temperature-induced changes in volume phase holographic gratings (VPHGs) recorded in the low-toxicity self-processing photopolymer poly(N-isopropyl acrylamide) (poly-NIPA) are reported on. Transmission and reflection gratings are exposed to temperatures ranging 8–60 °C to study the effect of temperature on their properties. First, the role of the photopolymer chemical composition is investigated by comparing layers containing NIPA with those containing acrylamide (AA) and measuring the normalized diffraction efficiency (DE) at 60 °C; higher thermal sensitivity is observed for poly-NIPA gratings (24% drop) versus low sensitivity for AA gratings (2% increase). The impact of the physical properties of the sensing layers (e.g., thickness/protective top layer) on their thermal response is studied. The reversibility of thermally induced changes in VPHGs is studied, especially the effect of exposure to the elevated temperature of 60 °C on the subsequent low-temperature response. The results reveal the significance of water desorption/absorption for the observed changes in poly-NIPA upon exposure to varied temperatures and indicate a thermally controlled memory effect. This effect is observed from DE values in transmission and from the spectral characteristics of the reflection gratings. A full reversibility of the DE and spectral characteristics is achieved at 8 °C.

1. Introduction

Photonic microstructures fabricated by holographic technologies are attracting significant interest and are aimed at facilitating the development of lightweight, cost-effective optical devices. Their potential practical applications among others are as holographic sensors,1–3 solar applications,4 lenses,5 holographic polarization optical elements,6 holographic displays,7 security holograms,8 data storage,9 interferometry,10 and anticounterfeiting.11 For all such applications the photosensitive material that is used to record holograms is a crucial component. For that reason, significant research work is dedicated to develop holographic recording materials with the desired properties. Among all the holographic recording media, photopolymers particularly have attracted much attention due to their appealing qualities such as large dynamic range, high diffraction efficiency (DE), high sensitivity, self-processing nature, and relatively low production cost.12

In recent years functionalized photopolymers have emerged as versatile holographic recording media that have the capability of holographic recording and additionally show a response to different analytes. Therefore, holograms recorded in such materials can be useful as a holographic sensor or indicator. To introduce the intended functionality in polymers, different approaches are utilized,2,13 and have been exploited for the fabrication of pressure,4,13,14 temperature,13,15 humidity,16 pH,15,17 glucose,18 and metal-ion sensors.13,19 One such approach uses a compositional variation of the photopolymer material before holographic recording. This is typically achieved by introducing suitably selected monomers,2,20 or nanoparticles,2,3,20 in the material. For example, the acrylamide (AA) monomer in the well-documented and widely studied AA-based photopolymer composition14,19,21 has been successfully replaced in different research studies with the diacetone acrylamide (DA) monomer22 and the N-isopropyl acrylamide (NIPA) monomer.23 This achieved better response of the holograms to pressure or temperature,13 and also lowered the toxicity of the polymer layers.

The NIPA-based photopolymer for holographic recording was first introduced by Leite.24 It was further optimized to record high-DE holograms in transmission (capable of up to 80% DE) and reflection mode (up to 20% DE) of recording.23 Its sensitivity to elevated temperatures was studied and documented13,22,23 in both types of holograms. Poly-NIPA is known as a thermosensitive polymer and is used in localized chemotherapy and hyperthermia,26 drug delivery,27 and water treatment.28 The high thermal sensitivity of poly-NIPA is attributed particularly to its hydrophobic-to-hydrophobic phase transition at a critical temperature. The lower critical solution transition (LCST) temperature occurs at ≈32 °C for pure poly-NIPA; however, this transition temperature can be tuned precisely within a wider temperature range using appropriate monomers in copolymerization with NIPA.29

On the capability of the NIPA-based photopolymer for use in holographic temperature sensor/indicator platforms that
can indicate changes in environmental temperature, different research studies have already been reported. However, further research work is still necessary to fully understand, effectively control, and address the temperature response of holographic sensors/indicators recorded in the NIPA-based photopolymer. This research work investigates in detail, to the best of our knowledge for the first time, the dynamics of temperature-induced changes below room temperature and the effect of temperature on the reversibility/memory effect of the induced changes. It studies the role of the main monomer, the influence of sensing layer physical properties such as thickness and presence of a top lamination layer (Melinex), on the temperature-induced changes in volume phase holographic gratings (VPHGs). The investigations focus on both transition and Denisyuk reflection gratings, thus measuring either the DE or spectral (color) variations on temperature, and test the possibility to recover to the original hologram characteristics after their exposure to elevated temperature.

2. Theoretical Background

2.1. Holographic Gratings

Holographic gratings are recorded by interfering two collimated coherent beams to produce a periodic pattern of light that induces a periodic variation in the optical properties (refractive index and/or absorption coefficient) of the recording layer. These gratings are classified into thin (surface/thin layers) and thick (volume) gratings depending upon the diffraction regime; this classification is particularly important as the two types behave differently. Most photopolymer holograms are volume phase holograms and for that reason, we focus on their properties. For example, thin phase gratings produce multiple diffraction orders and a sinusoidal grating can theoretically achieve a maximum DE of up to 33%. A thick phase grating obeys Bragg’s law and produces a single diffraction order beam when reconstructed with a probe beam incident at the Bragg angle. Their maximum DE can reach 100%. The work presented here is based on thick (volume) phase holographic gratings (VPHGs). They are recorded throughout the depth of a photosensitive holographic recording material (photopolymer) by spatially modulating its refractive index through exposure to an interference pattern created by two coherent recording beams. The period (and thus the special frequency) of VPHGs is achieved from adjusting the angle between the recording beams according to Equation (1).

\[
\lambda = 2n_0 \Lambda \sin \theta_B
\] (1)

\[
\frac{\Delta \eta}{\eta} = \frac{2}{\tan(\frac{\pi n_1 d}{\lambda_0 \cos \theta_B})} \frac{\pi n_1 d}{\lambda_0 \cos \theta_B} \left( \frac{\Delta n_1}{n_1} + \frac{\Delta d}{d} - \frac{\Delta \lambda}{\lambda} + \tan \theta_B \Delta \theta_B \right)
\] (3)

Here, \( \lambda \) is the recording beam wavelength, \( n_0 \) is the effective refractive index of the recording medium (photopolymer), \( \Lambda \) is the grating period, and \( \theta_B \) is the Bragg angle inside the medium.

The classification of holographic gratings is discussed in the literature and two main approaches are adopted utilizing either the Q-factor, applicable for gratings with relatively low refractive index modulation (RIM) or the \( \rho \)-parameter, applicable to gratings with very high RIM. Gratings operating as volume diffraction gratings are characterized by \( Q > 10 \) and \( \rho > 10 \). In this work, these values are respectively 136 and 76; therefore, the gratings are thick (volume) gratings. Kogelnik’s coupled wave theory (KCWT) provides an analytical expression for the DE of VPHGs. According to KCWT the maximum DE of transmission VPHGs at Bragg’s incidence for s-polarized light is determined by Equation (2).

\[
\eta = \sin^2 \left( \frac{\pi n_1 d}{\lambda_0 \cos \theta_B} \right)
\] (2)

The losses for non-s-polarized light at the spatial frequency used in this study (800 line mm\(^{-1}\)) are negligible and the difference in the DEs for the two states of polarization is less than 1%,\(^{[13]}\)

Here, \( \eta \) is the DE of the recorded transmission VPHGs, \( n_1 \) is the RIM achieved during recording, \( \Delta \) is the thickness of the grating, \( \lambda_0 \) is the probe beam wavelength, and \( \theta_B \) is the Bragg angle inside the medium.

2.2. Operation of the Holographic Sensor

The operation of holographic sensors discussed here is shown schematically (Figure 1). When the analyte-sensitive photopolymer layer containing the recorded holographic gratings is exposed to an external stimulus (e.g., temperature in this work), changes occur in the characteristics of the layer. In case of the holographic sensors based on volume transmission gratings, these changes take place in the thickness of the grating, grating period, and/or RIM, hence contributing to the effective change in DE, which is detected as an electronic readout of the ratio of the diffracted beam and probe beam intensities. For transmission gratings, the DE changes can be evaluated using Equation (3).\(^{[2,3]}\)

\[\text{Figure 1. Schematic illustration of the operation of holographic sensor: a) transmission and b) reflection.}\]
Here the terms \((\eta, n_1, d, \lambda_p, \theta_B)\) are the same as defined earlier and the terms \((\Delta n_1, \Delta n_0, \Delta d, \Delta \lambda_p, \Delta \theta_B)\) represent their respective changes. In our studies, the probe beam wavelength was kept constant, as well as the angle of incidence; thus, only the two terms related to the change in RIM and the thickness of the grating are expected to be the key contributors to the observed change of the DE of the transmission gratings. Here it is worth mentioning that the heating of the polymer layer may lead to its thermal expansion and thus swelling. In addition, because above the critical transition temperature the poly-NIPA layer changes its properties from hydrophilic to hydrophobic the layer expels water molecules and can experience shrinkage. Both dimensional changes can be also accompanied by a change in the RIM introduced during the recording of the hologram. Theoretical modeling of the properties of VPHGs\(^2\) reveals that typically the contribution of the RIM change to the change in DE is significantly smaller than the one of the dimensional changes.

The second type of holographic sensor studied in this article is based on the Denisyuk reflection hologram. It operates by producing a change in the color of the reconstructed holographic image when the layer is exposed to external stimuli. The color change is readable with the naked human eye and therefore, it is a focus of research for developing visual indicators and sensors. When quantified, this change in color can be detected as a spectral shift in the peak wavelength of the reflected light as given by Equation (4).\(^2,3\)

\[
\frac{\Delta \lambda}{\lambda} = \frac{\Delta n_0}{n_0} + \frac{\Delta \lambda}{\lambda} + \cot \theta_B \Delta \theta_B
\]  

Equation (4)

As described earlier, the exposure of the reflection sensor to elevated temperature can cause changes in the RIM as well as in the grating period. Since the probe angle is kept constant in the design of the interrogation system, only the first two terms will play a role in the observed spectral change. During heating/cooling of the layer, it is possible that the polymerized and unpolymerized regions of the holographic grating absorb and desorb water differently; thus, it is expected that an effective RIM also causes a contribution of spectral change in the peak wavelength.

3. Results and Discussion

3.1. Photopolymer Materials for Recording of Holographic Gratings

Figure 2 and Table S1, Supporting Information, show the compositions (A, B, and C) of the three photopolymers that were used in this study. Compositions A and B are used in the fabrication of temperature-sensitive transmission gratings, while composition C was optimized for the reflection mode of recording. Composition A is a modification of an AA photopolymer that has been previously used in other holographic applications.\(^1d,4b,21\) A reversible temperature response is reported for the AA-based photopolymer. After exposure to elevated temperature, the DE is observed to be within 2% of the original DE measured at room temperature.\(^13\) At the same time, an irreversible temperature response was detected in composition B upon exposure to a temperature of 60 °C, which is above the LCST. About 20% loss in DE was measured after cooling the sample to room temperature.\(^13\) This memory effect was further studied in this work to determine whether it can be controlled and even reversed by exposure to temperatures below room temperature. The two compositions A and B were used to compare their temperature response with the aim to further investigate the role of the monomers, while all other photopolymer components were identical. In composition A the main monomer is AA and in composition B the main monomer is NIPA and their concentrations in the solid polymer layer are identical. Composition C was used in the fabrication of a Denisyuk reflection grating to examine the memory effect in color changes and how it can be controlled.

To facilitate an easier comparison for the three photopolymers studied here, pie charts of the three compositions (A, B, and C) are shown (Figure 2). Compared with the first two compositions (A and B), composition C has a higher percentage of plasticizer and additionally it has a component citric acid, which is a chain transfer agent and enhances the recording performance of the photopolymer in reflection mode, as demonstrated in previously published work.\(^23\)

Transmission holographic gratings were recorded in compositions A and B using the optical setup in Figure 3a while Denisyuk reflection holographic gratings were recorded in Composition C.

![Figure 2](image-url)

Figure 2. The chemical composition of dry layers of AA- and NIPA-based photopolymer for fabrication of the holographic sensor. The exact amounts used to prepare the layers are available in Table S1, Supporting Information.
composition C with the help of the optical setup in Figure 3b. The thermal response of the holographic gratings was respectively studied by the setups shown in Figure 3c and in Figure 3d. A detailed description of the equipment is presented in the Experimental Section.

### 3.2. Study of Transmission Holographic Gratings

The following section presents the results from temperature studies of transmission gratings recorded with the help of the two-beam holographic setup shown in Figure 3a and tested with the help of the temperature-controlled setup shown in Figure 3c. Photographs of the physical samples and the recorded grating are shown in Figure S1a–e, Supporting Information. Examples of the real-time growth curve and Bragg selectivity curve of DE are provided in Figure S1f,g, Supporting Information. The DEs immediately after recording in different samples were measured to be in the range 35 ± 5%.

#### 3.2.1. Effect of the Main Monomer on the Temperature Response

The critical role of the NIPA monomer in the photopolymer material’s response to temperature variation was studied by exposing the VPHGs recorded in a reference AA-based (composition A) and NIPA-based (composition B) photopolymers to varying temperature in the range 8–60 °C. Results obtained from the temperature response of the VPHGs are shown in Figure 4. The dynamics of the change in the normalized DE (NDE) is measured as the samples experience four phases. First, the temperature is increased from 18 to 60 °C at a rate of 5 °C min⁻¹.
During the second phase, the sample remains at a constant temperature of 60 °C for 20 min. During phase three, the temperature is decreased from 60 to 0 °C at a rate of 5 °C/min. Finally, during phase four, the sample remains at 0 °C for 20 min (Figure 4a). It had previously been observed that DE changes are not instant, but they saturate within 15–20 min. For that reason, the time interval at the highest and the lowest temperatures was 20 min. Figure 4b shows the same data plotted with normalized DE (NDE) as a function of temperature. The NDE for Figure 4a and Figure 4b is taken as the ratio of the DE at the current temperature and the DE at the starting temperature 18 °C. The response of the gratings for the period where they were kept at constant temperatures 60 and 0 °C are shown, respectively (Figure 4c,d). In these two graphs, the DE values were normalized with their respective initial DE when the desired constant temperature was achieved.

The results in Figure 4a,b reveal a marked difference in the behavior of the two photopolymer formulations. Although the NDE for both gratings initially increases as the temperature increases, the rate of increase for the NIPA formulation soon slows in comparison to the AA formulation. In the next phase, while the temperature is kept constant at 60 °C, the NDE of the NIPA gratings decreases significantly and is still decreasing after 20 min. The gratings recorded in the AA-based photopolymer layers, however, show a minor increase in the same conditions. Therefore, the opposite behavior is observed here for AA and NIPA-based photopolymer gratings. The results also reveal that the changes in the AA photopolymer occur on a much shorter time scale. In the third phase, as the temperature is brought back down, the NDE of the NIPA grating decreases further, even speeding up the rate of decrease slightly. The AA and NIPA gratings have very similar trends here. Finally, in the fourth phase, as the temperature is kept constant at 0 °C, the NIPA gratings experience a significant increase, whereas the AA drops slightly.

When interpreting these results, it should be borne in mind that the grating recorded in the NIPA-based photopolymer layer response is a combination of the response of the basic photopolymer layer (seen in the AA layer curve) and the particular response of the temperature-sensitive poly-NIPA component. While the reference grating recorded in the AA-based photopolymer layer experiences swelling (increase of DE) with increasing temperature and shrinkage (decrease of DE) with the decreasing temperature, the opposite is expected for the grating recorded in the NIPA-based photopolymer layer. Above the LCST, the layer shrinks with increasing temperature (DE decreases) and below the LCST the layer will swell with increasing temperature (DE increases). Thus, since the responses are often in opposite directions, they will counteract each other to some extent.

The changes in the NIPA layer can be interpreted in light of the phase transition experienced by the polymer when passing through the LCST. The NDE changes with increasing temperature can be attributed to the hydrophilic–hydrophobic phase transition of poly-NIPA. As described in a previous study, up to 45 °C the poly-NIPA is likely to be in the hydrophilic state because the temperature is below the LCST of poly-NIPA and thus the behavior of the grating with increasing temperature...
is similar to that of the grating recorded in the AA-based photopolymer layer. The layer swells by absorbing water molecules from air, leading to a slight increase in NDE. This absorption leads to an increase in the thickness of the grating as well as an increase in the RIM of the grating recorded in the NIPA-based photopolymer layers due to the different amounts of water absorption in the polymerized and unpolymerized regions. At temperature above 45 °C, the NIPA-based photopolymer layer experiences a phase transition, switches to a hydrophobic character, and expels water molecules, which causes shrinkage and a drop of the RIM and thickness of the grating. This is observed as a decrease in the NDE.

During the cooling part of the temperature cycle (phase 3) there is a drop in the NDE of both AA and NIPA-based gratings and we see no increase of the NDE for NIPA as the temperature drops. This indicates some delay or irreversibility apparent in the dynamics of the NIPA switching process, which required further study. As the temperature reaches 8 °C, however, the trend reverses and during the final phase (20 min at 8 °C), an opposite response is again seen (Figure 4d). Figure 4c,d shows that there is a delay in the response of the grating due to the poly-NIPA being present in the photopolymer layer. Although there is little further change in the NDE for the reference sample (recorded in the AA-based photopolymer), once the preset temperature is achieved, the NDE of the grating recorded in the NIPA-based photopolymer layer continues to change during the 20 min real-time measurement. The curves shown in Figure 4 were measured in multiple samples, thus confirming the repeatability of the experiment.

3.2.2. Effect of Lower Temperature on the Reversibility of DE

The importance of the effect of exposing the sample to a temperature lower than the starting temperature on the reversibility of NDE was further investigated for NIPA gratings. The grating recorded in composition B was exposed to varying temperatures during the four phases. First the temperature was increased from 18 to 60 °C at a rate of 5 °C min⁻¹ during phase 1; then it was kept constant at 60 °C for 20 min in phase 2. In phase 3 it was decreased from 60 °C, but this time the final lower temperature was one of three: 18, 13, or 8 °C. In phase 4, it was kept at that final temperature for 20 min. The results are shown in Figure 5.

During the first three phases, the samples show very similar NDE changes as for the poly-NIPA sample in Figure 4. This demonstrates a good repeatability in the poly-NIPA grating response. The minor variations in NDE of samples compared to each other are most likely due to slight difference in thickness as the polymer layers are made by spreading photopolymer solution on a microscopic glass slide and an uncertainty of a few microns is noted in samples’ thickness. During phase 2 at 60 °C, the three samples show a sharp decrease in NDE most probably due to expelling water molecules when poly-NIPA becomes hydrophobic, as discussed in Section 3.2.1.

In phase 4, however, the behavior is markedly different. The large increase in NDE is only observed for the sample that is brought all the way down to 8 °C. This is clearly visible in Figure 5d, where the curves have been normalized and the staggered timing to the start of phase 4 is removed.

For the sample that is brought to 18 °C, we see no recovery at all in the 20 min for which the sample was observed.

Figure 5. NDE versus temperature for NIPA-based gratings with thickness of polymer layers $88 \pm 5 \mu m$. The symbols (,) represent temperature, NDE of NIPA gratings cooled to 18, 13, and 8 °C, respectively. a) Temperature and NDE versus time, b) NDE versus temperature, c) NDE dynamics at 60 °C, and d) NDE dynamics at lower temperatures 18, 13, 08 °C versus time. In (b) the solid symbols (,) show increasing temperature and the hollow symbols (,) show decreasing temperature.
This demonstrates that there is a memory effect of the grating exposed to elevated temperature (above the LCST of the polymer). This memory effect is smaller when the sample is brought to temperatures of ≅13 °C, and is fully erased once the temperature drops to 8 °C. It would appear that in these layers the poly-NIPA is unable to switch back to its original state unless a sufficiently low temperature is reached. In the 20 min duration studied, at 13 °C there is a small increase noted and the process of reversing the changes may be beginning.

3.2.3. Effect of Water Desorption/Absorption on the Temperature Response

The observed NDE changes are expected to be closely related to the ability of water desorption/absorption from/in the NIPA-based photopolymer layers. To investigate this, two sets of samples were investigated—one covered with a highly transparent plastic layer (Melinex) and the other uncovered, with the sample surface open to the air. The results are shown in Figure 6. The four phases in the temperature variation are the same as for Figure 4 in Section 3.2.1.

The most notable features are the differences observed in phase 2 and phase 4. In both phases we see that the behavior of the laminated NIPA grating is close to that of a grating containing no NIPA (see Figure 4)—purple curve for the AA grating recorded in the reference photopolymer with composition A. This is most likely because the effect of NIPA has been almost eliminated by the prevention of the movement of water molecules in and out of the layer. The difference in the NDE for laminated and nonlaminated layers, which could be related to desorption/absorption of the water molecules, is also shown (Figure 6a). The dynamics of water desorption at temperature 60 °C can be clearly seen during the second phase of the experiment—the process is completed after 10 min at 60 °C. During the cool-down cycle, at the rate of temperature change of 5 °C min⁻¹, the difference caused by the ability of the layer to absorb water is not very pronounced. It is clearly notable as soon as the sample reaches 8 °C temperature. These results confirm that water desorption/absorption is playing an important role in the temperature response of the grating recorded in the NIPA-based photopolymer. In addition, it confirms that the response of NIPA can be tuned by selecting a top layer with a suitable water permeability.

3.2.4. Effect of Photopolymer Layer Thickness on the Dynamics of Sensor Response

Next we investigate the effect of the photopolymer layer thickness on the poly-NIPA grating temperature response. VPHGs were recorded in transmission geometry at the same recording conditions as for the NIPA-based polymer (composition B) with layers of two different thicknesses — 88 ± 5 μm (thicker layer) and 43 ± 5 μm (thinner layer). Both sets of layers were exposed to the temperature range 8–60 °C under the same environmental conditions as in Section 3.2.1 and the DE was normalized similarly. The results are shown in Figure 7.

As shown in Figure 7a,b, the thinner layer shows a much larger response during the final phase. In phase 3, when the
temperature decreases, both the thicker and thinner layers show similar decrease in NDE as seen in Figure 7a,b. By dropping the temperature to 8°C, however, the ability to switch is again enabled. The NDE of the grating recorded in the thinner photopolymer layer increases dramatically and reaches more than double its original value measured at 18°C at the start of the experiment. Furthermore, it does not appear to have saturated after 20 min. The rate of NDE change in phase 4 is clearly dependent on the layer thickness, thus emphasizing the importance of this parameter for the sensor performance. We also note the very large magnitude of the NDE increase, which is probably caused by the larger relative dimensional change in the thinner layer.

The apparent difference in dynamics during the other phases is also of interest. The thinner layer appears to respond more quickly—for the thinner layer NDE decreases almost immediately in phase 1, and is flatter in phase 2, having already responded to the temperature change. In phase 3 neither layer switches back (Figure 7c), which indicates that the reversing of the change induced by the exposure to higher temperature is indeed related to achieving a specific switching temperature. In phase 4 the NDE for both begins to increase (Figure 7d), with faster dynamics again apparent for the thinner layer.

3.3. Study of Denisyuk Reflection Gratings

The effect of exposure to elevated temperature on the color change of the Denisyuk reflection holographic gratings recorded in the NIPA-based photopolymer (composition C) is investigated in this section. By exposing the holograms to the same temperature range studied in transmission holograms, we investigated the color change and its reversibility. This is important because it is one format in which indicator-type sensors are fabricated. The observation of the color changes in reflection holograms can indicate swelling and shrinkage in the layers. Denisyuk reflection gratings were selected for temperature study as their response can be observed after illumination with a white light source and therefore, they are comparatively easier in their use. Without the need of additional electronic read-out, one can observe by the naked eye the temperature-induced changes in the layer.

The photographic images of the object [percentage sign (%)] and results from the temperature study of the recorded Denisyuk reflection holographic gratings are shown in Figure 8. After recording with laser light of 532 nm wavelength and then bleaching the remaining photoinitiator with white LED light, samples were exposed to the same temperature cycle as described in Figure 4 with the addition of a final return to room temperature (18°C) at the end. This study on reflection gratings was conducted to double-check the observed switchable memory effect in transmission gratings exposed to elevated temperature.

As shown in Figure 8, when the reflection hologram experiences different temperatures the color of the reconstructed holographic image changes. This can be caused by a dimensional change (shrinkage or swelling of the layer) and a change in the effective refractive index of the layer caused by water desorption/absorption. As the typical contribution of the change in the effective refractive index of the layer to the observed spectral change is much smaller than the one caused by dimensional changes, we can interpret blue color in holograms as shrinkage.
in the photopolymer layer and green color as recovery toward the original spacing. Here we observe behavior that is very consistent with the adsorption and desorption of water molecules discussed in the previous sections. In phase 1, the temperature increases and the layer expels water, thereby shrinking and causing the hologram to reconstruct a blue color image. In phase 2, this blue color is maintained as the temperature is kept at 60 °C. In phase 3 as the temperature change is reversed, no reversal of the color change is yet observed, which implies that the sample exhibits a memory of its exposure to a temperature above the LCST. Consistent with the behavior seen in DE studies, the blue color remains until the temperature reaches 08 °C. As noted earlier in the DE studies, this is the temperature at which the reverse switching process appears to be enabled. After 10 min at this temperature, the green color begins to return and remains returning to room temperature.

A close color resemblance can be noted between the original hologram recorded (Figure 8b) and the hologram after the end of the temperature cycle (Figure 8j). The color reversibility of the hologram at such a lower temperature 8 °C for longer exposure indicates that the polymer matrix is potentially trying to achieve its original volume, which was at the start of the experiment at 18 °C.

By using a poly-NIPA-based photopolymer composition, we demonstrate that the photonic structure recorded in this material can be activated by exposure to a temperature above the LCST of the polymer. These results add to the field of active photonic structures such as those using optical metasurfaces and switchable polymer dispersed liquid crystal devices where different activation mechanisms are utilized. It must be noted that one of the limitations of the proposed structures is the activation mechanism, which requires uniform heating and implies a slow...
response time. One possible solution to this challenge is the incorporation of nanoparticles, which in the presence of external stimuli can heat up the materials locally. For example, in a previous study, gold nanorods were incorporated in a temperature-sensitive polymer—poly(N-isopropylacrylamide-co-N-isopropylmethacrylamide) and activated by illumination with an electromagnetic wave with wavelength 800 nm to switch between the hydrophilic and hydrophobic state and thus switch between the transparent and opaque state. The next step in the reported investigation is the holographic recording in magnetic-nanoparticle-doped poly-NIPA and to study the activation in an alternating magnetic field.

4. Conclusion

Investigation of the temperature sensitivity of VPHGs recorded in a NIPA- and AA-based photopolymer has been conducted over the temperature range 8–60 °C. The unslanted transmission and Denisyuk reflection holographic gratings were monitored by measuring their DE and color changes in the reconstructed holographic image, respectively. It has been established that substituting the AA monomer with NIPA in the polymer composition leads to enhanced thermal sensitivity. When the samples are left at the constant temperature of 60 °C, the DE drops by 24% in the case of the poly-NIPA-based grating due to hydrophilic-hydrophobic phase transition, whereas only a 2% DE increase is observed for the AA-based grating. The reversibility of the changes in DE of the poly-NIPA grating is shown to depend on temperature. A memory effect is observed at 18 °C, while partial and full reversibility of the temperature-induced changes are observed respectively at 13 and 8 °C. In additionally, blocking the sensor’s free exchange of water with the environment by covering the photopolymer layer with a plastic substrate decreases its sensitivity to temperature. These results confirm that the temperature dependence of the characteristics of poly-NIPA-based gratings is strongly related to water desorption/absorption by the photopolymer layer. Thickness effects on the sensor’s response time and the amplitude of change of the DE were also studied. It is demonstrated that the thickness of the layers can be used to tune the response time; as quicker response is observed in the thinner layers. Finally, the temperature effects on Denisyuk reflection gratings are displayed as color change from green to blue (reconstructed in white light). The temperature dependence of the reversibility of introduced color changes was confirmed. The observed temperature-sensitive response of poly-NIPA and/or of AA may be used for developing holographic temperature sensors/indicators visible in white light. Such sensors/indicators can be implemented over a wide range of applications; for example, they can be used in packaging labels where safe transportation of goods (food items, laboratory or electronic equipment) is required for protecting their quality against exposure to elevated temperatures.

5. Experimental Section

Chemical Materials Used in Preparation of Photopolymers: All chemicals (AA, NIPA, N,N-methylene bisacrylamide, polyvinyl alcohol, N-phenylglycine, erythrosine B, glycerol, citric acid) used in the photopolymer compositions were purchased from Sigma Aldrich and Fisher Scientific and used without further purification. Detailed exact formulations of the three compositions (A, B, and C) are available in Table S1, Supporting Information.

To prepare the binder polyvinyl alcohol (PVA) 10% w/v stock solution, 10 g of PVA was dissolved in 100 mL of deionized (DI) water by magnetic stirring and heating at 75 °C in laboratory conditions. The obtained solution was cooled to room temperature and used after filtering. To obtain a stock solution of the sensitizing dye, 0.11 g of photosensitive dye erythrosine B (ErB) was dissolved by magnetic stirring in 100 mL of DI water at room temperature to prepare a dye solution of concentration 0.11% w/v. Finally, to prepare the photopolymer solutions, all components were thoroughly mixed in a glass beaker with magnetic stirring for 1–2 h at laboratory conditions (relative humidity, RH, 36 ± 5% and temperature 23 ± 2 °C) until a fully homogeneous solution was obtained.

Preparation of the Photopolymer Layers: To use the prepared photopolymer solutions for holographic recording, layers were made by depositing a certain amount of solution and evenly spreading on the microscopic glass slide (dimension 7.6 cm × 2.6 cm × 0.1 cm). First, the slides were placed on a leveled surface and after coating with the photopolymer they were allowed to dry in a dark room for 12–16 h at laboratory conditions (RH of 36 ± 5% and temperature 23 ± 2 °C). With 1.5 and 0.75 mL solution (grating period 1.25 mm) and 16 h at laboratory conditions, the samples were kept for about an hour in the holography laboratory to equilibrate the samples with the room environmental conditions.

Recording Transmission Holographic Gratings: In transmission mode (Figure 3a), VPHGs were recorded in the photopolymer materials (composition A and B) by using two collimated recording beams obtained by splitting laser light from a Nd:YVO4 (532 nm) with a polarizing beam splitter (PBS). The state of polarization of the reference beam was rotated using an additional half-wave plate (HWP) in the path of the reference beam; this was conducted to ensure that both recording beams (reference and object) had the same polarization state (s-polarized), thus providing the condition for maximum visibility of the interference fringes. The angle between the recording beams was set to have a recording spatial frequency of 800 lines mm−1 (grating period 1.25 μm). During the holographic recording, the photopolymer layers were exposed for 100 s to the interference pattern of beams having a diameter of 13.0 mm with a total recording intensity of 3.8 MW cm−2.

During recording, the real-time development of the holographic gratings was monitored by measuring their DE growth curves using a 632.8 nm probe beam from a helium–neon (He–Ne) laser. This was conducted to ensure that the recording process was carried out appropriately. Bragg selectivity curves of the recorded gratings were obtained by rotating the recorded samples placed on a computer-controlled rotational stage (Newport ESP300) and probing with the 632.8 nm beam. The diffracted beam intensity (I0) was monitored with an optical power meter (Newport Model 840) for growth as well as Bragg curves and LabVIEW computer software being used to plot the acquired data of DE in real time while the probe beam incident angle was varied by ±3° from the Bragg angle. Bragg selectivity curves were measured to ensure that the gratings were unslanted and no overmodulation effects in the thicker layers were taking place.

In monitoring the recording of transmission gratings, the DE value was calculated as the ratio of the diffracted beam intensity (I0) and the incident beam intensity (I). The initial DE of holograms recorded in different samples was measured in the range of 35 ± 5%. After recording, the transmission gratings were bleached by exposure to ultraviolet (UV) light in a Dymax UV-curing system (model ECE-200) for 100 s with the UV exposure intensity of 60 mW cm−2. This was conducted to polymerize the remaining monomers left in the layer as it was previously demonstrated that UV curing helps to stabilize the recorded gratings. In Figure S1c,d, Supporting Information, pictures are shown for the samples after UV exposure. A photograph of the transmission hologram recorded in the NIPA layer...
is displayed in Figure S1e, Supporting Information. Examples of the real-time growth curve of DE for the transmission hologram recorded in AA, NIPA layers and the Bragg selectivity curve of DE are shown in Figure S1f,g, Supporting Information. In addition, the surface morphology of the grating structures was studied utilizing atomic force microscopy (AFM). The obtained results are shown in Figure S2, Supporting Information, for NIPA gratings a,c,e and AA gratings b,d,f. The grating period obtained from images a,b for AA and NIPA gratings, respectively, is $\approx 1.25$ μm. As can be seen, the surface relief amplitude is very small; thus, no significant contribution to the DE of the grating is expected. The photoduced spatial variation of the refractive index of the layers was observed by phase contrast microscopy and the results are shown in Figure S3, Supporting Information. Due to limitations in the resolution to the phase contrast microscope, the results shown in Figure S3, Supporting Information, are for gratings with spatial frequency of 300 and 450 lines mm$^{-1}$.

**Recording Denisyuk Reflection Holographic Gratings:** In reflection mode, the Denisyuk reflection holographic gratings were recorded in the photopolymer material (composition C) using laser light from Nd:YVO$_4$ (532 nm) as in the setup in Figure 3b. For recording the photopolymer layer was kept very close to the object and tilted slightly with a small angle ($\approx 5^\circ$) to avoid overlap of the reflected and reconstructed beam in readout. During recording, layers were exposed for 100 s to the interference pattern formed by the incident and reflected beams with total recording intensity 25 mW cm$^{-2}$. After recording reflection gratings were bleached in white LED light, by keeping them under an LED light source for a few hours. The mechanical stability of the optical setups during recording was ensured using a floated optical table (Newport RS 4000).

**Study of the Thermal Response of Transmission Holographic Gratings:** To study the temperature response of the recorded VPHGs, they were exposed to different temperatures ranging from 8 to 60 °C, while at the same time the DEs of the gratings were monitored. The temperature range was selected to include the critical solution temperature, which for pure NIPA is 32°C, the lower limit was determined by conditions where no water condensation on the surface of the layer was observed. The upper limit of the temperature range was chosen to be 60°C to achieve well-observable change in the gratings' initial DE (at least 5%) for a relatively short time. The temperature was increased and decreased at a rate of 5 °C min$^{-1}$. The experimental setup used in the temperature response study of transmission VPHGs is shown in Figure 3c. The recorded VPHGs were placed on the temperature-controlled stage (Linkam Model PE120 stage), and the temperature of the stage was increased/decreased in a controlled manner with the help of a temperature controller (Linkam Model T96-P LinkPad system controller). The setup is capable of controlling temperature in the range $-25$ to 120°C with accuracy of ±0.1°C. During the temperature exposure, changes in the intensity of the first order diffracted beam ($I_1$) and intensity of the transmitted beam ($I_0$) were monitored simultaneously for calculating the DE changes. The DE in this experiment was calculated as $I_1/(I_0 + I_1)$.

**Study of the Thermal Response of Denisyuk Reflection Holographic Gratings:** For investigating the temperature response of the Denisyuk reflection gratings recorded in the composition C photopolymer, the temperature-controlled stage (Linkam Model PE120) was utilized to vary the temperature in the range 8–60 °C while changes in the hologram characteristics at specific temperature were observed from the visible color changes of the hologram. The temperature was increased and decreased at a rate of 5 °C min$^{-1}$. The hologram was illuminated with a white LED light as shown in Figure 3d and during reconstruction photographs were taken with a digital camera (SONY Model SEL1855).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors acknowledge the financial support provided by the TU Dublin Fosraigh Dean of Graduate Students Award and are thankful to FOCAS, TU Dublin, for the use of equipment and facilities. The authors are also thankful to Mr. Karl Gaff (Technical Officer, School of Physics and Clinical & Optometric Sciences, TU Dublin) for his assistance with Figure 3c.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

Denisyuk reflection hologram, N-isopropyl acrylamide (NIPA)-based holographic indicators/sensors, photopolymers, temperature-sensitive gratings, volume phase holographic gratings

Received: March 2, 2021
Revised: May 14, 2021
Published online:

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