SELF-INSCRIBED WAVEGUIDE ARRAYS

IN SOFT PHOTOPOLYMERS

SELF-INSCRIBED WAVEGUIDE ARRAYS IN SOFT PHOTOPOLYMERS: FROM DYNAMIC LENSES TO MATERIALS THAT COMPUTE WITH LIGHT FILAMENTS

BY

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A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF MCMASTER UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY IN CHEMISTRY

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Hamilton, Ontario, Canada

TITLE: Self-Inscribed Waveguide Arrays In Soft Photopolymers: From Dynamic Lenses
To Materials That Compute With Light Filaments
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NUMBER OF PAGES: xxx and 192

<u>Abstract</u>

Nonlinear optical processes have been used for many years to cause light to behave in unique ways. These can influence various aspects of the light beams, including the spatial intensity profile. More specifically, a naturally divergent beam can maintain its initial beam profile when propagating through a nonlinear medium due to the increased refractive index causing focusing. This process is called self-trapping and can be elicited for both coherent and incoherent light in a number of nonlinear media. Analogous to this, modulation instability (MI) is a nonlinear process that causes a broad beam of light of break up into a large population of self-trapped filaments. When these processes occur in photopolymers, light guiding structures are inscribed within the material and persist even after the light is removed. Our group has previously studied the behaviour and interactions of light undergoing self-trapping and MI in photopolymer systems.

The studies presented in this thesis show novel interactions between multiple incoherent beams undergoing MI, utilization of these interactions, as well as the development of new polymeric systems capable of inducing MI. The filaments produced when orthogonal beams underwent simultaneous MI would align with themselves, forming highly ordered structures within the material. These interactions were used as the basis of an encoding and computing system based on the specific ordering of the resulting filaments. The mechanical properties of the resulting polymers were improved and tuned by developing a long-chain organosiloxane based system. The embedded waveguide structures are capable of guiding light when significantly deformed and restore to their initial parameters. A hydrogel system was also developed that was capable of producing

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self-trapping and MI with incoherent light. The samples were tested with biological systems and were also used to produce dynamic lens samples with enhanced angle of view.

Acknowledgements

I would firstly like to thank my supervisor, Dr. Kalai Saravanamuttu, for allowing me to work in her research group and providing wonderful support throughout my graduate studies. Your passion for research has always inspired me to explore any new ideas that I may have and to keep trying even if something fails. I appreciate the time you took over the years to offer advice and guidance to me, as well as giving me the opportunity to develop as a scientist and a professional. I would also like to thank my committee members, Dr. Michael Brook and Dr. Ignacio Vargas-Baca, for their support and knowledge that has been key to the development of my projects.

Thank you to all the members of the Saravanamuttu group, both past and present. You have each helped throughout this process with your insight, advice, and support. Special thanks to Matt for working alongside me and for putting up with me through all those experiments in the basement. Many thanks to Derek, Kathryn and Fariha for your friendship, support and endless discussions, both scientific and non-scientific. Additional thanks to Liqun, Kailash, Dinesh, Chris, Hao, Ian, Oscar and Amy for the conversations and insight over the years. I would also like to thank Krystle, Eva, Thomas, and Kyle for allowing me to supervise you and develop alongside you. Thank you to the rest of my friends at McMaster, especially Lucia for all of the coffee breaks and keeping me entertained.

I would like to thank Meghan Stearns as well. The love and support you have shown is what has motivated me throughout my studies. I don't know where I would be if I had not met you at McMaster and conjured up the courage to speak to you. Thank you for

V

always being by my side, I love you so much. I would also like to thank all my family and friends that have supported me over the years, especially my siblings, Katie and Matt, my grandpa and grandma, and the Stearns family.

Finally, I would like to thank my parents, Theresa and Steve Hudson, for always believing in me and encouraging me to chase my dreams. I would not be where I am now had it not been for your love and support. Thank you for taking the time and effort over the years to listen, provide help, and show love to me. I dedicate this thesis to my father, who encouraged me to stay in school for as long as I could. I hope I have made you proud.

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List of Abbreviations

BFL	Back focal length
CCD	Charge-coupled device
DCM	Dichloromethane
DEGDA	Diethylene glycol diacrylate
DMEM	Dulbecco's Modified Eagle Medium
EY	Eosin Y
FBS	Fetal bovine serum
FFT	Fast Fourier transform
FITC	Fluorescein thioisocyanate
FL	Focal length
FWHM	Full width at half maximum
HEMA	Hydroxyethyl methacrylate
MAPTMS	3-(Trimethoxysilyl)propyl methacrylate
MI	Modulation instability
NEAA	Non-essential amino acids
NIH3T3	National Institute of Health 3-day transfer, inoculum 3×10^5 cells
NIR	Near infrared
NLS	Non-linear Schrödinger
NVP	N-vinyl pyrrolidone
PBS	Phosphate buffered saline

PEG	Poly(ethylene glycol)
PEGDA	Poly(ethylene glycol) diacrylate
QTH	Quartz tungsten halogen
Silmer	3-(Polyoxyethylene)propylheptamethyltrisiloxane
TEA	Triethylamine
TEOA	Triethanolamine
λ_{em}	Fluorescence emission wavelength
λ_{ex}	Fluorescence excitiation wavelength
λ_{max}	Maximum wavelength
n	Refractive index
Δn	Change in refractive index

1 Introduction

1.1 **Optical self-trapping and modulation instability**

1.1.1 Nonlinear light propagation

Waves, including light, travelling through a linear dispersive medium will experience a natural broadening during propagation^{1–3}. For beams of light, this occurs due to the change in spatial frequency of waves travelling off from the optical axis. This arises from their individual phase velocity⁴. This phenomenon is referred to as diffraction and will occur to varying degrees depending on the coherence and size of the beam^{5–7}. It can be advantageous, however, to nullify this diffraction to study the behaviour of light beams over long distances and for variety of applications, such as communication. The most common practice to counteract light's natural diffraction is through the total internal reflection of it within a high refractive index channel (known as a waveguide). However, these waveguides are typically fixed structures that limit investigations into dynamic phenomena that can occur between multiple beams of light^{8,9}.

An alternative method to counteract diffraction is the propagation through a nonlinear medium^{10–12}. In these materials, the dielectric constant, and thus the index of refraction (*n*), will increase proportionally in the presence of light. This can produce a number of different optical phenomena including self-phase modulation^{13,14} or mode-locking¹⁵ but in terms of minimizing diffraction, the self-focusing effect is of greatest interest. As the beam propagates through the medium, the high intensity centre of the beam will generate the greatest change in refractive index. This results in the focusing of light into this region and suppression of the light's diffraction.

1.1.2 Self-trapping of a light beam

If there is a balance between this self-focusing effect and the natural diffraction, the beam will propagate through the material without changing its beam profile and is classified as self-trapped^{4,16–22}. The self-trapped beam generates a gradient waveguide within the medium that it itself is confined within.



Figure 1.1 Illustration showing the change in profile of a beam of light, over time [from bottom to top], as it (A) diffracts, (B) undergoes self-focusing, and (C) is self-trapped.

In order to understand the dynamics occurring, this phenomenon can be expressed using a nonlinear Schrodinger equation. If we consider a beam with an electric field amplitude ε propagating along the z-axis, we can use the paraxial wave equation to model its behaviour within a nonlinear material. In this case, we get²³:

$$2ik_0n_0\frac{\partial\varepsilon}{\partial z} + \nabla_{\perp}^2\varepsilon + 2k_0^2n_0\Delta n\varepsilon + ik_0n_0\alpha\varepsilon = 0$$
(1.1)

where k_0 is the free space wavenumber, n_0 is the initial refractive index of the material, $\nabla_{\perp}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$, and Δn is the change in refractive index along the propagation path. The first term in the equation represents the beam's propagation, while the fourth

term corresponds to attenuation due to the material. More relevantly, the second and third terms show the direct competition between the natural diffraction of light and the photoinduced refractive index change, respectively.

1.1.2.1 Self-trapping of incoherent light

Initial studies of self-trapped beams (also referred to as spatial solitons) utilized coherent light exclusively^{4,24} and it was considered necessary to produce the effect. However, extensive experimental and theoretical studies have shown that under certain conditions, partially^{18,20,21,25,26} and fully incoherent light^{22,27,28} can be self-trapped. In order to achieve this, specific conditions are required for the medium; the timescale of its nonlinear response must be significant slower than the random fluctuations that occur in the incoherent beam. In the case where these two timescales are comparable, the medium will now be able to respond to each fluctuation or "speckle" in the beam and will cause the beam to break up into small fragments. However, with a slower nonlinear response, the beam appears time-averaged, and therefore uniform, to the medium and will generate a smooth waveguide capable of confining the entirety of the beam. This slow response can be achieved in photorefractive crystals^{17,22,26} by using an initially low intensity beam (as the material's response is proportional to the intensity) or in photopolymers^{28–30} by using a system with a slow enough rate of the reaction.



Figure 1.2 Evolution of a self-trapped incoherent white light beam over time in a photorefractive crystal. Reprinted by permission from **RightLink**: **Springer NATURE** Self-Trapping of Incoherent White Light, Mitchell, M.; Segev, M. © 1997

1.1.3 Modulation instability of a light beam

A number of additional phenomena can be elicited through the interaction of light with a nonlinear medium. One of these is modulation instability (MI), a universal process that occurs in a variety of nonlinear wave systems^{31–39}. During MI, small perturbations in the continuous wave become amplified due to the competition between the nonlinearity and natural dispersion. For light waves, these perturbations arise in the amplitude^{37,40,41} or

phase^{36,42} of the beam. Light that undergoes MI during propagation will break up into filaments (spatial regime) or pulse trains (temporal regime), with the individual characteristics identical to each other and determined by the corresponding property of the parent beam.

Since they arise from the same competition, self-trapping and MI are closely related. This is emphasized in the spatial regime, where the filamentation that occurs during MI causes the broad beam to become an array of spatial solitons. This understanding allows for MI to be expressed by a nonlinear Schrodinger equation comparable to the one used to model self-trapped beams^{43–45}. Initial solutions to MI in light were determined for the temporal domain, where different frequency components generate the pulse train break up. These solutions can be translated to the spatial domain due to analouges existing between the two. More specifically, plane waves propagating at some angle with respect to each other correspond to the frequency components²⁴. The interference pattern generated by these waves is what eventually leads to soliton formation.

An equation to model the beam in x propagating along z can be expression as below¹⁹:

$$2i\frac{\partial A}{\partial Z} - \frac{\partial^2 A}{\partial X^2} - 2k_0 l_D \partial nA = 0 \qquad (1.2)$$

where A(X,Z) is the beam envelope, $Z = z/l_D$, $X = x/x_0$, k_0 is the wave number, $l_D = n_0 k_0 x_0^2$ is the diffraction length, ∂n is the refractive index change, x_0 is the transverse scale, and n_0 is the linear refractive index. By applying a modulation to the initial conditions of the beam comparable to that produced by the interference pattern, we see break up of the optical field as it propagates along z. The fringes produced show an
increase in peak intensity and narrowing in profile similar to self-trapping, with the strength of this change dependent of the nonlinear response of the material.

1.1.3.1 Modulation instability of incoherent light

For years, it was generally believed that the process of MI was a coherent one; the initial modulation arises from interference between coherent beams of light. However, upon the theoretical and experimental discovery of incoherent solitons, investigations into the existence of incoherent MI were pursued^{46–53}. Theoretical models were first developed using partially spatially incoherent light and showed that using a slow-response nonlinear medium, as is used for incoherent solitons, allows the time averaged light intensity to respond to the induced refractive index change⁴⁶. It was seen that MI would only occur when the balance between the nonlinearity and the relative coherence of the beam exceeds a defined threshold.

Intriguing, however, was the discovery of MI in "white" (fully temporally and spatially incoherent) light. Because of the lack of coherence in both domains, the theories used for partially incoherent light cannot fully describe the generation of white light solitons. Therefore, Segev et al. developed a theory that could take into account the fluctuations, especially in the temporal domain, of the incoherent beam and show the existence of MI in the beam⁵¹. They showed that there remains a threshold for instability as seen for partially coherent light, that there exists a collective effect among the temporal frequency where they all participate in the breakup of the beam above the threshold value, and these elements will self-adjust to match the spatial modulation of this collective instability process.



Figure 1.3 Temporal evolution of MI in a broad beam of incoherent white light propagating through a photorefractive crystal. From Kip, D.; Soljacic, M.; Segev, M.; Eugenieva, E.; Christodoulides, D. N. *Science* 2000, *290*, 495–498. Reprinted with permission from AAAS.

Experimental evidence of MI was discovered for both partially incoherent light as well as white light using the parameters outlined by their corresponding theories^{48,50,52,54}. In both cases, the predicted properties of incoherent MI were observed: a noninstantaneous nonlinear refractive index change with a response time slower than the fluctuations in the beam is required, and there exists a threshold depending on the properties of the beam before MI occurs. For partially incoherent light, once the nonlinearity of the medium surpasses the threshold, the beam spontaneously breaks up into an array of one-dimensional filaments⁴⁷. The periodicity of these filaments is dependent on both the coherence of the light and the magnitude of the nonlinearity. With

white light, comparable spontaneous pattern formation will occur with the beam breaking up into an array of filaments. However, there is also confirmation of the prediction that white light MI is a collective effect with respect to the temporal elements of the light⁵². Due to the threshold value being frequency dependent for partially incoherent light, as seen both theoretically and experimentally, one could expect multiple periodicities to arise in the resulting arrays when white light undergoes MI as it consists of a large range of frequencies. As predicted by Segev et al., however, the frequencies instead act collectively and a single threshold value exists across the temporal spectrum^{51,52}. This gives the fascinating result of nearly identically sized filaments emerging from a strongly uncorrelated light source.



Figure 1.4 Demonstration of the different frequencies that make up white light acting collectively and exhibiting a single threshold for MI. Reprinted figure with permission from Schwartz, T.; Carmon, T.; Buljan, H.; Segev, M. Spontaneous Pattern Formation with Incoherent White Light. *Phys. Rev. Lett.* 2004, *93* (22), 223901. Copyright 2018 by the American Physical Society.

1.1.4 Materials which elicit a nonlinear optical response

The majority of optical systems we encounter on a daily basis use materials that have

a linear relationship with light. In these instances, when light interacts with the material,

the properties of both are independent of each other and so no inherent changes occur^{7,55}. The molecules of the material do not change, and thus there is no change to its dielectric polarization, and simply re-emit any light that acts upon it. The resulting light will have the same frequency as the incident and will only be reflected or deflected.

However, there exist cases where, usually in the presence of high intensity light, a nonlinear response occurs in the material. Some of these responses have been outlined in 1.1.1 but others include changes in the frequency (ie. second harmonic generation) or polarization of the light^{10,11}. In all of these cases, the dielectric polarization of the material will change in the presence of the electric field of the light. The polarization (P) can be expressed as¹⁰:

$$\tilde{P}(t) = \varepsilon_0 \left(\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots \right)$$
(1.3)

where ε_0 is the permittivity in free space, χ is the susceptibility factor, and *E* is the electric field. Under linear conditions, only the first term of the equation contributes and thus we see the polarization is proportional to the electric field and the susceptibility is independent of the field. When particular material or intensity parameters are satisfied, however, the higher order terms influence the polarization and nonlinear responses will occur. These higher order terms correspond to different types of nonlinear responses from the medium; second order effects include second harmonic generation and Pockels effect, while Raman scattering and Kerr effects are third order^{10,56,57}.

To generate self-trapping or MI, a change in the refractive index is the desired nonlinear response. For this reason, materials where the Pockels or Kerr effect is elicited are used; these are both electro-optic effects that cause a refractive index change in the

presence of an electric field^{10,11,58-60}. The Pockels effect shows a linear proportionality between the refractive index change and the electric field and only occurs in materials that lack inversion symmetry in their crystal structure. The Kerr effect, however, exhibits a refractive index change that is proportional to the square of the electric field. This effect can occur in all materials, with no symmetry limitations, and can also be elicited by the electric field of the light itself. A particular class of materials that exhibit these effects, referred to as photorefractive media, have electrons excited to a higher energy band upon illumination⁶¹⁻⁶⁴. When the medium is non-uniformly irradiated, the excited electrons will preferentially diffuse from the bright to the dark areas to balance the net charge. This resulting charge distribution will generate the refractive index change via the electro-optic effect.

1.1.4.1 Nonlinear materials for incoherent self-trapping & modulation instability

As previously mentioned, a slow response nonlinear material is required to facilitate soliton formation in incoherent light. While other nonlinear effects have been seen in a multitude of different types of materials, such as semiconductors⁶⁵, gases^{66,67} and glass^{68,69}, this response time limitation changes the focus to more dynamic systems. These materials behave as instantaneous Kerr media and require high intensity light to elicit the different nonlinear effects. Segev et al. found a resolution to this with the discovery of spatial solitons in photorefractive crystals⁶¹. The key attributes of the medium that allows for incoherent self-trapping are its intensity-dependent response time and use of a nonlocal external electric field to elicit the electro-optic effect. Because the applied field dictates the extent of the refractive index change, beams with significantly lower power

can be used. Furthermore, the response time of the material can be tuned to exceed the rate of perturbations in the incoherent beam by controlling the intensity, as they are inversely proportional to each other. Initially they were able to generate self-trapping with partially spatially incoherent light using a SBN crystal, maintaining the beam's initial diameter throughout the length of the crystal, but were also able to achieve this for incoherent white light in the same medium.



Figure 1.5 Top-down photographs of a light beam undergoing self-trapping in a photorefractive crystal. Reprinted figure with permission from Mitchell, M.; Chen, Z.; Shih, M.; Segev, M. Self-Trapping of Partially Spatially Incoherent Light. *Phys. Rev. Lett.* 1996, 77 (3), 490–493. Copyright 2018 by the American Physical Society.

Due to the overlapping mechanisms underlying the two phenomena, the attributes required to facilitate incoherent self-trapping can also be applied to MI^{46–48,50–53,70}. Specifically, the intensity-dependent response time in a photorefractive crystal is desired to allow the material to see the time-averaged profile of the broad beam. Segev et al. determined both theoretically and experimentally the specific requirements needed to elicit this response and discovered a distinct difference between coherent and incoherent MI^{46,47}. There exists a distinct threshold for the nonlinear refractive index change to generate incoherent MI. This threshold is dependent on coherence properties of the beam

and does not exist in coherent MI. When the thresholds for these key parameters, response time and refractive index change, are satisfied, the partially incoherent beam will break up into arrays of 1D and 2D filaments. This also holds true for white incoherent light with the added observation that it is a collective effect with respect to the temporal spectrum (the whole of it undergoes MI at the same threshold value) and each frequency self-adjusts to match the threshold value for the overall process⁵².

1.1.5 Nonlinear incoherent light forms in photopolymers

Photorefractive crystals were the primary medium to experimentally study incoherent self-trapping and MI when initially discovered. However, it was later demonstrated that other systems capable of achieving a comparable response time could produce these phenomena, including photoisomerizable polymers^{71,72} and liquid crystals^{25,73,74}. One of particular interest is a photopolymerizable system^{28,53,75–78}. In these, a photo-initiated chemical reaction occurs within a large population of identical chemical species (ie. monomers) and causes long chains to be formed. The required refractive index change to generate nonlinear optical effects is produced by an increased localized density of atoms during the formation of these long chains. Specific properties of the resulting material can be tuned based on the chemical composition of the photopolymer (these will be discussed further in a later section). Most importantly for incoherent self-trapping and MI, however, is that the initiation process of the photopolymerization is dependent on the intensity of light used on the medium^{28,75}. This allows the response time of the material to be controlled and satisfy the requirements to elicit these phenomena.

Photopolymer systems can be differentiated from other nonlinear optical mediums due to the formation of permanent structures within the medium due to its interaction with light^{75,77,79,80}. These structures emerge due to the nature of the chemical reaction that forms the polymer chains. The structures initially form due to the densification of the material that causes the refractive index change, and are permanent due to the irreversibility of the chemical reaction. Since the regions of increased refractive index are retained within the material, the structures are able to continue guiding light after initial irradiation. These self-written waveguides have been investigated further to better understand their formation and are being used to develop complex materials with relatively simple manufacturing procedures^{81,82}.

In our group, we have conducted extensive research into the relationship between nonlinear processes, specifically self-trapping and MI, and photopolymers. Self-trapping of both coherent and incoherent light within an organosiloxane polymer system has been observed, along with the dynamic of these beams^{28,29,79,83,84}. Furthermore, MI of incoherent broad beams of light has been used in a variety of photopolymer systems to facilitate the formation of different permanent light guiding structures^{77,78,85,86}.



Figure 1.6 Optical micrographs of a photopolymer sample with an embedded structure generated by MI. Reprinted (adapted) with permission from Burgess, I. B.; Shimmell, W. E.; Saravanamuttu, K. Spontaneous Pattern Formation Due to Modulation Instability of Incoherent White Light in a Photopolymerizable Medium. *J. Am. Chem. Soc.* **2007**, *129* (15), 4738–4746. Copyright 2007 American Chemical Society.

1.2 Interactions of self-trapped beams

The natural progression of studies into self-trapped beams is to look at how multiple beams can interact with each other. Unique behaviours can arise depending on the inherent properties of the solitons, some of which only occur in the spatial regime^{87–90}. Despite this, the phenomena are universal with respect to the different mechanisms capable of generating self-trapped beams. Of particular interest is the orientation and directionality of the beams with respect to each other and the communicative effects that arise based on this.

1.2.1 Parallel propagation of spatial solitons

A diverse range of soliton interactions can occur when they are travelling along a parallel path. These interactions primarily depend on the response time of the medium,

the phase difference and the separation distance between the two solitons⁴. The first factor determines whether the interaction will be coherent or incoherent in nature. This follows similar guidelines to the formation of solitons, where the relationship between the timescale of the interference generated by overlapping beams and the medium's response time dictate which type of interaction occurs. For coherent collisions, either the response time is instantaneous (thus making the dependence on timescale insignificant) or the relative phase of the interference remains stationary for longer than the response time. Both allow the medium to see and be influenced by the interference effects. Incoherent collisions occur when the response time is much slower than the interference occurring in the overlapping regions.

The phase difference will dictate whether the solitons will be attractive or repulsive upon collision⁹¹. In coherent collisions, in-phase solitons will attract while out-of-phase pairs will repel due to constructive and destructive interference, respectively. Incoherent collisions are attractive since the medium cannot respond to the phase difference and will instead respond to the intensity overlap. These interactions are further complicated, however, when the separation distance of the solitons is taken into account. The behaviours described above occur when the solitons are in close proximity (relative to their size) and there is significant overlap in their phase or intensity. However, depending on the nonlinear mechanism of the material, solitons separated by a far enough distance may interact differently than expected. This is particularly noteworthy for incoherent solitons as repulsion (initially believed to be exclusive to coherent collisions) can be elicited in photorefractive or photopolymerizable mediums at particular separation

distances⁸³. This occurs because of diffusion of the nonlinearity to the solitons and a resulting dark region between them, causing the two to repel.

1.2.2 Non-parallel propagation of spatial solitons

With a strong understanding and supporting evidence of the parallel interactions, investigations into non-parallel propagation were conducted^{87,92,93}. These include angled beams that are either in-plane or out-of-plane with respect to each other, as well as orthogonally propagating solitons. Angled beams give rise to interesting phenomena including the steering and spiralling of solitons, both of which can be controlled by the relative incident angle^{94,95}. For orthogonal solitons, however, research into their collisions has been limited. This is partially due to the anisotropic nature of a large majority of the nonlinear materials used to produce spatial solitons. This has lead to the use of photoresponsive isotropic media to investigate their behaviour⁹⁶. Primarily, a photoisomerizable polymer is used as the model system to simulate the orthogonal collision of coherent beams⁹². By controlling the phase, position and intensity of a control beam, up to four beams propagating perpendicular to the control beam could be affected. Fusing, steering and dispersion of the beams can be achieved depending on the initial parameters of the control beam.

For non-parallel incoherent collisions, investigations have been limited to angled beams; there has been no specific research into orthogonally propagating incoherent beams. However, the results from the angled beams can infer the expect behaviour of this interaction. It has been shown that when two incoherent solitons are angled at some degree greater than their critical guiding angle, they will undergo a fully elastic

collision⁹³. This means the beams will simply pass through each other and is true independent of whether they are copropagating or counterpropagating. Because orthogonally propagating solitons satisfy these same parameters, one would expect fully elastic collisions to occur.

1.2.3 Modulation instability filament interaction

As with single solitons, the primary focus of broad beam interactions has been coherent interactions between co- and counterpropagating beams^{57,97}. Theoretical experiments have shown the beams will influence each other via cross-phase modulation and results in transverse modulation instability. However, most of these studies do not investigate collisions occurring between multiple populations of solitons generated during MI. Our group has conducted research into the ordered structures formed in photopolymers when multiple white light beams undergo simultaneous MI using photomasks⁷⁷. During this study, an interesting result was seen where filament alignment occurred along the propagation axes of the beam despite there being no modulation of the beam. This result implies some sort of spontaneous alignment of filaments, which will be investigated further.

1.3 **Properties of polymers**

Research interest in polymers, both in the past and currently, is incredibly vast because they offer a hugely diverse range of properties that can be obtained by tuning different aspects of their chemical nature^{98–101}. These long chain molecules consist of one or more monomer species bonded together in various ways. Property changes are primarily achieved through changes to the initial monomer(s) used but can also be

affected by alterations to the various steps of the polymerization reaction. These changes can result in polymers with different average molecular weight, dispersity, crosslinking or linearity, which in turn dictates the bulk properties of the material.

1.3.1 Factors affecting polymer properties

The most critical factor that determines the resulting polymer's properties is the choice of monomer. The inherent chemical structure of the monomer will dictate how the polymerization takes place, how adjacent units or chains will interact, and how the resulting chains with interact with their environment⁹⁹. For example, hydrophobic monomers will typically result in polymers with very low wettability. Monomers commonly fall into two categories based on the polymerization method they undergo: chain-growth or step-growth. For chain-growth polymerization, an initiator species reacts with the monomers, which typically contain a carbon-carbon double bond, to generate an active species. The initiator species are generated in various ways, including heat or light¹⁰². Additional monomers react with the active species to propagate the chain growth of the polymer until a termination step occurs. Step-growth monomers are able to react without an initiator (although the presence of a catalyst is common), forming shortchained oligomers that can further react with each other to generate longer chains. Because of this, the reaction does not terminate and remains active even after all the monomers have been consumed. Unique polymer backbones can be obtained by polymerizing two monomer species (from the same category) together¹⁰⁰. Depending on the conditions of the reaction, these copolymers can have either a random arrangement of the monomers, distinct blocks of each connected together or anything in between. This

can change not only the physical properties of the resulting material but also the microscopic arrangement. The length, arrangement and chemical nature of each block can dictate a change in a number of properties that are otherwise difficult to alter in homopolymers, such as morphology, crystallinity, and thermal stability.



Figure 1.7 Illustration of the different configurations for copolymers.

Outside of the building blocks of the polymer, the specific characteristics of the polymer chains also greatly influence the material. Specifically, the length of the polymer chains as well has the connectivity between them have a strong influence on these properties. Characterization of the chain length can be conducted using two measurements: average molecular weight and the polydispersity. The average molecular weight can be used in conjunction with the molecular weight of the monomer(s) to find how long the chains are on average. This is because the monomer molecular weight is

well defined and gives an accurate factor to divide the polymer chains by. The average molecular weight is determined in two ways: by taking the number average (M_n), or by taking the mass average (M_w). These values individually, however, do not provide any indication of the distribution of chain lengths, which can be very wide for non-controlled polymerization reactions. The dispersity, D, is a measure of the heterogeneity of the molecules and thus can provide this information. It is calculated by taking the quotient of the mass average and number average molecular weights¹⁰³. Because the mass average molecular weight is always greater than the number average (as it is more sensitive to higher molecular weight chains), D will always be equal or greater than 1. A completely uniform polymer population will have D = 1 as the two molecular weight measures will be identical.

In terms of the connectivity, properties of the polymer will be significantly dictated by the arrangement of monomers and the number of connections to each chain. Stiffness and rigidity can be increased in a polymer by adding a chemical that is capable of bonding two or more polymer chains together. These species are called cross-links and depending on their length, concentration, number of connections and chemical nature, their impact on the resulting material's rigidity can change^{104–106}. Cross-links can be introduced either during the polymerization, with an additional monomer containing multiple polymerizable groups that can react with different chains as they form, or after polymerization, by reacting a molecule between the polymer chains or substituents off of them. The measure for the degree of crosslinking within a polymer is the crosslink density, quantified as the ratio between the molecular weight of uncrosslinked polymer

and polymer between crosslinks and is often determined via swelling measurements^{105,107,108}. Because the cross-links have such a large impact on the mechanical properties of the polymeric material, changing the crosslink density often becomes the first handle to tuning these properties.

1.3.2 Physical properties of polymers

A number of physical properties are studied to characterize the feasibility of polymeric materials as well as investigate the relationship between these properties and their chemical nature. The correlation between the two is prominently seen in the physical state of the resulting material. There are three main factors that determine which state the polymer will be in after polymerization: chain length, crosslink density, and chain interactions^{98,99}. Although the each one's effect on the state is known, there is no fixed threshold value for them; the relative value of each combines to determine which form the material will take. Polymers with longer chain lengths tend to be hard solids whereas shorter chain lengths give a softer material that may be liquid. Congruently, polymers tend to be solid with a higher cross-link density and liquid at lower values. Both of these trends originate from the fact that more covalent bonding has occurred in the material and thus is more strongly held together. The final factor, chain interactions, relies on the monomers and the non-covalent interactions between them, such as hydrogen bonding. When chains come in close proximity to one another, these attractive forces come into play and can increase the rigidity of the material and thus, can result in a solid polymer. There are additional factors, such as the conformation and configuration of the polymer chains, which tie into these interactions and their relative strength.

The physical state, however, only gives a very broad overview of the underlying physical properties. It is therefore important to understand the more specific measures and to characterize the material based on these. For liquid polymers, rheology is used to quantify the viscoelastic properties of the material and provide insight into its movement and resistance to force¹⁰². Solid polymers cannot flow, so it is difficult to perform rheological studies on these materials. Therefore, more traditional mechanical measurements are used to characterize them, including tensile and compressive strength, Young's modulus, and hardness⁹⁹.

Each measure gives specific insight into the different ways to deform the material. The tensile strength, for example, refers to the material's ability to resist failure upon elongation. By stretching a sample with uniform dimensions, the amount of force required to break it can be measured and used to determine the tensile stress, and thus the strength. These same principles apply to the compressive strength, except the force is applied inward and the polymer is now compressed rather than elongated. Determination of the compressive strength (in general) can be more difficult than the tensile strength as the sample tends to buckle and thus, the force is not uniform across the sample¹⁰⁹. Young's modulus is able to use the tensile strength, along with the strain, to measure the elasticity of the material and determine its resistance to deformation. There are additional properties that can be measured, such as the flexural strength and the fatigue, which can be combined with the first three to give an overview of the bulk physical strength of the material. Local strength throughout the material can be inferred from other mechanical measurements, including the hardness. Hardness is the material's resistance to indentation

and is usually linearly related to the mechanical strength^{110–112}. It is measured by pressing a small point (of varying shapes) into the material and determining the force required to make an indent with it. The different indenter shapes (including Rockwell, Shore, and Brinell) can be used depending on the inherent properties of the material and their susceptibility to indentation. More specifically, Rockwell durometers (the device used to measure hardness) are used for harder plastics whereas Shore durometers are used for soft elastomers¹¹³.

1.3.3 Optical properties of polymers

The underlying principles that dictate the optical properties of polymers are based on how individual atoms and molecules interact with light¹¹⁴. It was initially found that individual molecules exhibit a molar refraction that is dependent on its molar mass¹¹⁵. This relationship also had additive properties, meaning the total refractive index of the molecule is a summation of the refractive power of each of the substituents within it. This relationship has been expressed in a number of ways, but one of particular interest is a simplified one formulated by Lorenz and Lorentz^{116,117}:

$$n = \sqrt{\frac{1+2\frac{R}{V}}{1-\frac{R}{V}}}$$
(1.4)

where *n* is the refractive index, *R* is the molar refraction, and *V* is the volume of the molecule. This equation can be applied to polymers since it is additive and thus by using the molar refraction and volume of the monomer¹¹⁴. An increase in refractive index can be generated via the polymerization reaction because of changes to the molar refraction and volume when going from the initial monomer to the individual units in the polymer

chain. This can be translated to polymer blends, where the refractive index is determined based on not only the chemical structure of each monomer but also their relative percentage within the blend. A number of additional optical properties can be determined based on the chemical structure of the polymer. These include birefringence, which requires specific crystallinity to the polymer or through flowing the material¹¹⁸, light scattering, which can be used to determine average molecular weights^{119,120}, and nonlinear optical properties which have been previously outlined.

Other properties exist for polymeric materials that are based less on the specific chemical structure of the monomers and more on the bulk chains and the processes used to generate them^{103,114}. Colour and transparency are two significant ones that fall in this category and can be considered volume properties. This is because they are dictated by changes within the total volume of the polymer sample. Transparency in particular is strongly impacted by the generation of crystalline regions within the material¹²¹. These can form when long chains are able to fold and stack into lamellae, which can occur naturally or be induced through nucleation or stretching^{122,123}. These regions will strongly scatter light and so a high population of them will prevent light from transmitting through the material. A polymer is considered opaque when the light transmittance through it is 0%. Materials with a value greater than that, but less than 90%, are classified as translucent.

1.3.4 <u>Hydrogels</u>

Hydrogels are a class of polymeric materials that are able to retain a large volume of water^{124–126}. The crosslinked polymer network of the hydrogel does not dissolve in water

and will instead swell in the presence of it. They can be generated using natural or synthetic polymers and are quite versatile, with their physical (ie. flexibility, softness, etc.) and chemical (ie. water retention, opacity, etc.) properties being highly tunable. Because of their favourable properties, hydrogels have been researched in a wide range of fields that aim to exploit these properties for specific applications, including biomedical devices^{127,128}, tissue engineering¹²⁹, and agriculture¹³⁰.

The driving force behind the swelling nature of hydrogels is the presence of hydrophilic groups in the polymer backbone; these groups will bind water that has infiltrated the polymer network¹²⁴. This bounded water will push out on the network as it builds up, resulting in swollen material. The total degree of swelling is dictated by the opposition of forces driving water flow into the material, like the osmotic and capillary forces, and the forces restricting the network generated by the crosslinked polymer chains.

The polymer networks used to form the hydrogel are divided into two different classes: permanent or reversible¹²⁶. Permanent hydrogels are formed when strong, covalent chemical crosslinks are produced between the polymer chains, while reversible hydrogels form when physical interactions, such as ionic or hydrogen bonding, lead to network formation. Depending on the polymer backbone and type of crosslink used to form the gel, different characteristics can be introduced such as stimuli-responsiveness and biodegradability.

Quantifying the degree to which a hydrogel can swell is critical in many of the applications they are used for. This is because they are reliant on the water content the

samples are capable of reaching and maintaining. There are multiple methods for the determination of the swelling ratio for hydrogels, but the most common practice is to compare the dried and swelled weight of a hydrogel sample. The equation used to calculate the ratio is¹³¹:

$$R_s = \frac{W_s}{W_d} \qquad (1.5)$$

where W_s is the weight of the swollen hydrogel sample, and W_d is the weight of the sample when dried. The kinetics of the water uptake can also be quantified using dynamic properties such as the rate of approach to equilibrium and the transport mechanism.

The physical and optical properties of hydrogels are measured in much the same way as other polymeric materials. The main difference is the submergence of the hydrogel sample in temperature-controlled bath during testing¹³². This allows for determination of the samples' properties in its equilibrium-swollen state. To tune these properties, the chemistry of the polymer network or the degree of swelling can be altered^{133–136}. The composition and length of the polymer chains that make up the network will have a direct correlation to the resulting hydrogel, much in the same way as bulk polymers. Specific examples include the addition of a crosslinking agent increasing the tensile strength¹³⁷ or a higher molecular weight decreasing the opacity of the gel¹³⁸. The degree of swelling also has a significant effect, as the material gets softer and more transparent when swollen. However, this is difficult to control without external stimuli so is used less often to change the hydrogel's properties¹³⁹.

1.3.4.1 Transport of molecules into hydrogels

The mesh-like structure of the polymer network within hydrogels means that watersoluble molecules that are small enough can migrate into the sample. This property is critical to a number of applications hydrogels are used for, especially drug delivery^{140,141} and cell scaffolding^{142–144}. Molecules can diffuse through the water and are able to penetrate the hydrogel matrix as long as the pores within the mesh are big enough. The rate of diffusion into and out of the hydrogel is governed by the size and mobility of the polymer chains as well as any interactions between the chains and the diffusing molecule^{145–147}. Additionally, the polymer volume fraction will also significantly impact the diffusion as more polymer in the hydrogel means there is less water, and therefore less solution for the solute to move through¹⁴⁵.

A number of different compounds have been used as the solute, including fluorescent dyes^{144,146}, specific drugs^{141,148}, and even macromolecules¹⁴⁹. The chemical nature of the polymer network is tuned to minimize interactions with the molecule while the conditions of the solution, such as temperature and pH, are regulated to maximize mobility. Furthermore, detailed analysis of the dynamics involved in this diffusion can be achieved by localizing the source of solutes^{144,150}. By studying the gradient formed as they diffuse from one side of the sample to another, a better understanding of the relationship between diffusion and concentration can be ascertained.



Figure 1.8 Fluorescent images of unidirectional diffusion of a dye into hydrogels of different composition. Reproduced in part from Wei, D.; Xiao, W.; Sun, J.; Zhong, M.; Guo, L.; Fan, H.; Zhang, X. A Biocompatible Hydrogel with Improved Stiffness and Hydrophilicity for Modular Tissue Engineering Assembly. *J. Mater. Chem. B* **2015**, *3* (14), 2753–2763 with permission of The Royal Society of Chemistry.

1.3.4.2 Interactions with biological systems

As previously mentioned, because of the high water content and permeability of hydrogels, they serve as an excellent platform to design cell scaffolds for tissue engineering^{143,151,152}. They are able to encapsulate the cells and mimic the extracellular matrix by providing structural stability and nutrient transport to the cells. Optimization of the hydrogel material is required for this purpose, as the cells have not only a desired stiffness and porosity for the extracellular matrix, but may also require additional chemistry on the hydrogel to enhance their adhesion. Depending on the mesh size and substituents on the polymer backbone, cells may be able to migrate and proliferate through the hydrogel, which becomes important for tissue engineering¹⁵³. Certain hydrogel networks can also be designed such that enzymes in biological systems break them down and leave just the encapsulated cells¹⁵⁴.

Particular cell types prefer to orientate themselves during growth, such as muscle or nerve cells. Patterning the substrate the cells are grown on can further enhance this effect^{155–158}. The cells respond to the chemical or stiffness gradients (or both) introduced by the patterning and will proliferate accordingly. This patterning is introduced into

hydrogels in various ways but most predominately through photolithography or photomasking^{159–161}. This causes a change in chemistry in the irradiated areas, either by increasing the degree of polymerization or causing a bioadhesive molecule to bond to the polymer network, which the cells respond to and brings the hydrogel closer to replicating the natural matrix.



Figure 1.9 The growth of a rat dorsal root ganglia cell into a photo-induced modified channel in an agarose hydrogel, shown via (a) optical microscopy, (b) confocal fluorescence microscopy, and (c) fluorescence microscopy. Reprinted by permission from RightLink: Luo, Y.; Shoichet, M. S. A Photolabile Hydrogel for Guided Three-Dimensional Cell Growth and Migration. *Nat. Mater.* 2004, *3* (4), 249–253. © 2004

1.4 **Dynamic optical lenses**

Traditional imaging systems make use of plastic or glass lenses and mechanical parts to be able to focus onto specific objects. By moving either the object or the lenses, the focal plane can be moved and different regions within a sample can be imaged¹⁶². However, the mechanical parts make it difficult to miniaturize these systems; optical systems found in nature, in contrast, do not use this translation¹⁶³. Instead, they rely on soft optical components that can change focal point via deformation. This has led to the design of tunable lenses that rely on a variety of different mechanisms to cause the deformation^{164–167}. Most commonly, these tunable lenses are comprised of a liquid that is interfaced with either a second, immiscible liquid or a thin polymer film. The focal point is then changed by controlling the curvature of this interface, typically electrically, electromechanically or by pumping liquid in or out of the chamber. Optical systems have been designed with lenses on the order of millimetres in diameter that can easily switch between a double convex configuration to a double concave and obtain a focal point anywhere between 0 and 80 mm¹⁶⁴. Advantageously, flexible light sensors can be adhered directly to the polymer films to give a wide-angle field of view as the film is stretched¹⁶⁷. A more recent advancement for focal tunable lenses is the use of hydrogels as the lens material and changing the focal point by controlling the degree of swelling, typically with an external stimulus^{168,169}.

1.5 <u>Summary</u>

The fundamental physics that occur when beams of incoherent light undergo selftrapping and modulation instability are well established^{51,52,54}. Exploring different materials that are capable of eliciting these responses has led to the development of unique methods to generate microstructures^{53,77,78,85}. These methods also rely on interactions that occur between solitons as they propagate alongside and through each other. A class of materials capable of this is photopolymers, with the formation of long chains causing the desired refractive index change¹¹⁴. Polymers can be specifically tuned to generate materials with desired mechanical and optical properties by controlling their inherent chemistry^{98,99}. Beyond this, different classes of polymers exist that are capable of

unique behaviours, such as hydrophilic polymers that can uptake water and swell to significantly higher volumes^{124,126}.

The thesis presented here has two primary focuses: investigate the interactions that occur between beams undergoing MI, and utilize MI in unique applications. The first research objective of the thesis is to investigate and better understand the interactions that occur between multiple incoherent beams as they undergo MI in a photopolymer (Chapter 2). The impact these interactions have on the filaments formed during MI is focused on, along with the resulting structures formed in the polymer. The generation of distinct patterns based on filament alignment that can be used for optical encoding and computing systems is then be demonstrated (Chapter 3).

The second focus is explored further by inducing MI and self-trapping in new photopolymer systems. The aim is to generate large arrays of light-guiding channels with improved mechanical properties and added functionality. This is first investigated using a modified organosiloxane copolymer system that is highly tunable in terms of flexibility and hardness (Chapter 4). This allows for the embedded structure to continue guiding light even with significant deformation. The second system explored is a photopolymerized hydrogel, where the response of the embedded structure in relation to the swelling of the material is studied (Chapter 5). Overall, the thesis presents significant advancement in the understanding and practicality of nonlinear light propagation based fabrication method.

1.5.1 Contributions

For the work presented in Chapter 2, Matthew Ponte and I contributed equally. We were responsible for running and analyzing the single beam, two beam, and three beam experiments, and for writing the manuscript. Ponte, Saravanamuttu, and I were responsible for writing the manuscript. I was additionally responsible for running the three beam, non-orthogonal experiments and analyzing the results.

For Chapter 3, Matthew Ponte and I contributed equally to the manuscript. Ponte, Mahmood, Saravanamuttu, and I were responsible for writing the manuscript. Ponte and I were responsible for designing the experiments, running the $2^2 X 2^2$ experiments, and performing the FFT analysis. Ventura and I were responsible for designing and running the encoding experiments, and analyzing the results. Mahmood and I were responsible for designing and running the arithmetic experiments.

In Chapter 4, I was responsible for designing and running the optical experiments, conducting the compression tests and analyzing the results. Brook, Saravanamuttu and I were responsible for writing the manuscript. Bacus, Whinton, and I were responsible formulating the different compositions of the polymer system.

Finally, for Chapter 5, Saravanamuttu and I were responsible for writing the manuscript. I was responsible for running the functionalization of PEG reaction and formulating the hydrogel system. I was also responsible for optimizing the optical experiments, developing the dynamic lenses and performing the swelling analysis. Eva Chang and I were responsible for running experiments to determine the effect of pH and preliminary testing with biological cells.

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2 <u>Self-organized Lattices of Nonlinear Optochemical Waves</u> <u>in Photopolymerizable Fluids: the Spontaneous Emergence</u> <u>of 3-D Order in a Weakly Correlated System^{*}</u>

2.1 Abstract

Many of the extraordinary three-dimensional architectures that pattern our physical world emerge from complex nonlinear systems or dynamic populations whose individual constituents are only weakly correlated to each other. Shoals of fish, murmuration behaviours in birds, congestion patterns in traffic and even networks of social conventions are examples of spontaneous pattern formation, which cannot be predicted from the properties of individual elements alone. Pattern formation at a different scale has been observed or predicted in weakly correlated systems including superconductors, atomic gases near Bose Einstein condensation and incoherent optical fields. Understanding pattern formation in nonlinear weakly-correlated systems, which are often unified through mathematical expression, could pave intelligent self-organizing pathways to functional materials, architectures and computing technologies. However, it is experimentally difficult to directly visualize the nonlinear dynamics of pattern formation

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in most populations – especially in three dimensions. Here, we describe the collective behaviour of large populations of nonlinear optochemical waves, which are poorly correlated in both space and time. The optochemical waves - microscopic filaments of white light entrapped within polymer channels - originate from the modulation instability of incandescent light travelling in photopolymerizable fluids. By tracing the threedimensional distribution of optical intensity in the nascent polymerizing system, we find that populations of randomly distributed, optochemical waves synergistically and collectively shift in space to form highly ordered lattices of specific symmetries. These, to our knowledge, are the first three-dimensionally periodic structures to emerge from a system of weakly-correlated waves. Their spontaneous formation in an incoherent and effectively chaotic field is counterintuitive but the apparent contradiction of known behaviours of light including the laws of optical interference can be explained through the soliton-like interactions of optochemical waves with nearest neighbours. Critically, this work casts fundamentally new insight into the collective behaviours of poorly correlated nonlinear waves in higher dimensions and provides a rare, accessible platform for further experimental studies of these previously unexplored behaviours. Furthermore, it defines a self-organization paradigm that, unlike conventional counterparts, could generate polymer microstructures with symmetries spanning all the Bravais lattices.

2.2 Introduction

Nature is imprinted with patterns that are breathtakingly diverse in composition, selfengineered functionality, dimensionality, dynamism and scale.^{1–6} Several mechanisms have been proposed to explain the spontaneous emergence of patterns and symmetry

breaking in homogeneous systems, which predominantly take place under nonlinear conditions.^{2,7} Modulation instability (MI) is an exceptionally wide-reaching mechanism that describes the spontaneous emergence of patterns from the galactic to atomic length scales.⁸ In this stochastically driven process, noise - negligible perturbations in the otherwise homogeneous system - becomes greatly amplified under nonlinear conditions. Resulting patterns range from the spiral waves of galaxies⁹, Aelian ripples in sand^{10,11}, turbulent flames¹², breaking ocean waves¹³ to trains of matter-wave solitons in Bose Einstein condensates¹⁴ and populations of bright light filaments.¹⁵ Although spectacularly varied in dynamics, composition, function and scale, these processes are unified through mathematical expression of MI based typically on the Nonlinear Schrödinger Equation (NLS).¹⁶ Optical fields suffer MI through a particularly striking process; in the spatial regime, a broad, uniform beam travelling through a photoresponsive medium becomes unstable and collapses into discrete filaments of light. Each filament is a nonlinear wave, which like its relative, the spatial soliton, propagates without changing shape or intensity.¹⁷ This non-divergent propagation originates from competition between the natural diffraction (and divergence) of a light beam and self-focusing caused by the nonlinear photoresponse of the medium.

We previously showed that the MI of optical fields can be efficiently coupled with photochemical systems; for example, broad, uniform beams of light travelling through photopolymerizable fluids spontaneously divide into tens of thousands of bright filaments - each entrapped within its own microscopic polymer thread.^{18,19} Similar behaviours have recently been reported in polymer blends.^{20,21} The mechanism underlying MI in these

systems has been extensively studied and characterized.^{18,19} Briefly, MI occurs when noise inherent to the system – weak, normally negligible inhomogeneities in the optical field or the photopolymerizable fluid become amplified during polymerization. Noiseinduced minor variations in the refractive index changes associated with polymerization seed the growth of filaments – the preferential concentration of optical intensity. A synergistic process results in which each filament grows by inducing a polymer channel along its path and populating this evolving cylindrical waveguide – a potential well - as optical modes. Because they are seeded by adventitious noise, MI-induced filaments (and waveguides) are randomly distributed in space but possess statistically identical diameters;¹⁸ such amplification of a select length-scale or frequency is characteristic of MI.¹⁷ We previously showed that the characteristics of the filaments (density, width) – consistent with theoretical descriptions of $MI^{22, 23}$ - are only affected by the coherence of the optical field²⁴. Experimental studies moreover showed that although the rate of MI increased with intensity, the widths of the resulting filaments (diameter = $76 \pm 3 \mu m$) remained statistically identical¹⁸.

Critically, our studies revealed that nascent polymerizing systems elicit MI in weakly-correlated fields including incandescent light, which is incoherent in both time and space. The MI of incoherent light was first discovered in a photorefractive crystal;^{25,26} until then, it had been considered exclusive to coherent fields. An incandescent beam is a chaotic²⁷ system of visible and NIR waves, which are poorly correlated in phase and amplitude; the beam consequently is an ensemble of intensity speckles, which fluctuate randomly in space at the *fs* timescale.²⁸ Due to their inherently slow response to light (*ms*)

to *s*), photopolymerization systems do not see this fragmented wavefront and respond instead – like the human eye - to a time-averaged, smoothed profile of the beam. It is this fundamental property of noninstantaneity, which facilitates MI of incoherent beams.

The MI of incandescent light in photopolymerizable systems provides a rare and valuable experimental platform to study the interactions of nonlinear waves, which govern pattern formation in weakly-correlated fields - under the precisely controllable environment of an optics experiment. This could in turn provide new insight into the collective behaviours of other weakly-correlated but less-tractable systems ranging from charge density waves, superconductors and atomic gases.¹⁷ MI and pattern formation in incoherent optical fields has been extensively studied in a single dimension -i.e. with one optical beam propagating along a fixed axis;²⁹ ordered structures have been generated by externally imposing patterns through amplitude masks, for example.^{18, 33-34} However, the objective of probing MI and pattern formation in higher dimensions has not until now been possible. Here, we describe first-time studies of the collective behaviour in 2-D and 3-D of multiple, non-parallel populations of nonlinear incandescent waves propagating in a photopolymerizable medium. By tracing the distribution of optical intensity within the medium, we acquire richly sensitive insight into the dynamics of these interactions, the remarkably collective behaviour of these weakly correlated nonlinear waves and the spontaneous self-organization of the initially homogeneous polymerizable fluid into highly ordered, 3-D architectures with different symmetries.

We generate very large populations of nonlinear incoherent waves – self-trapped filaments - through the MI of incandescent beams propagating through a

photopolymerizable sol. The sol, which consists of oligomeric siloxanes bearing methacrylate substituents,³⁰ is sensitized to the blue-green spectral region ($\lambda_{max} = 460 \text{ nm}$) with titanocene molecules. When exposed to incandescent light (370 nm - 1000 nm), the titanocenes generate biradicals, which initiate the free-radical polymerization of methacrylate groups.³¹ Consequent changes in the refractive index (Δn) of the medium satisfy the stringent prerequisites to elicit nonlinear incandescent waveforms¹⁷ including self-trapped beams^{28,32} and filaments.^{18,19,22} The most critical of these prerequisites is a noninstantaneous photoresponse: the *ms* to *s* timescales associated with polymerization exceed the *fs*-scale, phase fluctuations characteristic of the incandescent field, which is spatially and temporally incoherent -i.e., has poor correlation of phase and amplitude in space and time. The medium therefore responds to only the time-averaged profile of the beam and is unaffected by its rapid and random fluctuations.^{17,28,32} Methacrylate polymerization moreover generates a saturable, relatively large Δn (~0.006), which entraps the entire modal population and wide spectral range of incandescent light^{17,28,32}, enabling this entire incoherent and fragmented wavepacket to propagate *collectively* as a nonlinear wave. This Δn arises from the chemical change and densification of material during polymerization, whose initiation rate is directly proportional to the intensity of incident radiation³³.

To elicit MI, we irradiate a transparent cuvette containing fluid organosiloxane sol (cm^3) with up to three collimated, broad and mutually perpendicular incandescent beams (X, Y, Z) emitted by three identical Quartz Tungsten Halogen (QTH) lamps (Figure 2.1; see 2.10.1). For each of the three types of experiments (single beam, two beams and three

beams), we experimentally determined the optimum intensity to be the value at which MI generated filaments that were well defined (in terms of width and maximum optical intensity) and in the case of multiple populations, exhibited long range self-organization. We found that the optimum intensity per beam decreased with the number of beams from 7.1 mWcm⁻² (single beam) to 4.1 mWcm⁻² (two beams) to 2.4 mWcm⁻² (three beams). This is because at t = 0 s, the medium is extremely sensitive to the superposed (cumulative) optical intensity from multiple beams. When the intensity of each beam exceeds the optimum value, the medium undergoes rapid polymerization to form a uniform monolith. In this case, the medium is entirely insensitive to the random fluctuations (noise) that are critical to trigger the onset of MI (see Introduction). Spatial intensity profiles of Beams X and Z at their respective exit faces were imaged onto high-resolution CCD cameras and monitored over time.



Figure 2.1 Optical assembly employed for experiments of modulation instability in photopolymerizable fluids. Beams (X, Y, Z) emitted by three perpendicularly positioned quartz-tungsten-halogen (QTH) were each collimated $(L1_x, L1_y, L1_z)$ and launched into a transparent cuvette (10 mm³) containing photopolymerizable fluid (S). Spatial intensity profiles of the beams at the respective exit faces of Beams X and Z were imaged through a pair of plano-convex lenses (L2, L3) and imaged onto CCD cameras.

2.3 <u>MI of a single incandescent beam: a population of randomly distributed</u> <u>filaments</u>

A single incandescent beam (X) launched into the organosiloxane sol undergoes MI and spontaneously collapses into a large population of high-intensity filaments. These filaments -nonlinear waves of incandescent light – that propagate along the x axis without diverging¹⁸, are randomly distributed in space. Figure 2.2(a-e) traces the spatial intensity profile of Beam X after it was launched into the medium: the beam illuminates the entire entrance face ($\sim 1 \text{ cm}^2$) of the sample, propagates over 10 mm and at t = 0 s, appears uniform at the exit face (Fig. 2.2b). It then rapidly becomes unstable due to MI.^{18,22} which is seeded by adventitious and normally negligible noise in the system. Originating from small inhomogeneities in the optical field or the fluid organosiloxane sol, noise becomes amplified by the evolving Δn in the medium so that by t = 1650 s, Beam X has spontaneously transformed into a large population ($\sim 8,000 \text{ cm}^{-2}$) of stable and statistically identical (diameter = $76 \pm 3 \mu m$)¹⁸ filaments (Fig. 2.2c, e).^{18,34} These filaments inscribe and become entrapped as optical modes within channels of high Δn – cylindrical waveguides, propagate through the medium without diverging and appear as high-intensity peaks at the output. The non-divergent nature of self-trapped filaments has also been detailed in our previous study of the MI of single beams¹⁸ and is further confirmed through optical micrographs, which provide direct evidence of cylindrical waveguides induced by filaments (*vide infra*). Because they originate from noise, filaments (and waveguides) have no long range ordering in the yz plane (Fig. 2.2c) as confirmed by the absence of high frequency peaks in the corresponding FFT spectrum

(Fig. 2.2d, see 2.10.2 for procedure). In a separate experiment, Beam Z propagating alone in the same medium suffers MI at t = 2035 s to form an equivalent population of filaments, which propagate along the *z* axis and are randomly distributed in the *xy* plane (Fig. 2.2f-j).



Figure 2.2 Modulation instability (MI) of individual incandescent beams launched along the *x* axis (Beam X) (a-e) and in a separate experiment, along the *z* axis (Beam Z) (f-j) of a photopolymerizable sol. The spatial intensity profile of Beam X was imaged at the sample exit face (represented by red square in (a)) and monitored over time. Profiles acquired (b) before and (c) after MI are presented together with the (d) corresponding FFT. The (e) 3-D beam intensity profile after MI highlights the high-intensity, discrete self-trapped filaments. Corresponding and equivalent images for Beam Z are presented in (f-j). All scale bars = 200 μ m.

2.4 <u>Simultaneous MI of an orthogonal pair of incandescent beams: a stack of 2-D</u> filament grids with square symmetry

By strong contrast, the two populations of filaments self-organize into a periodic stack of 2-D square lattices when Beams X and Z *simultaneously* undergo MI (Figure 2.3). The strong correlation in the positions of filaments in this arrangement is strikingly different from the random distribution of filaments propagating with only parallel counterparts (Fig. 2.2). In the case of two orthogonal populations, the filaments spontaneously shift in space and collectively converge into the same set of *xz* planes that are stacked along the *y* axis. Each plane is a 2-D grid composed of mutually orthogonal filaments that intersect multiple times as they propagate along the *x* (Fig. 2.3a-e) and *z* (Fig. 2.3f-j) axes, respectively. At the exit faces of Beams X and Z (corresponding to the *yz* and *xy* planes), these co-planar filaments form rows that are stacked along *y* (Fig. 2.3c, e, h, j). High frequency peaks in the corresponding FFT spectra show that stacking occurs along the *y* axis with long range ordering and an average inter-row periodicity of 69 μ m (see 2.10.2 for procedure); the spectra also confirm that there is no long range ordering along the *x* or *z* axes (Fig. 2.3d, i).

The self-organized filaments permanently inscribe the corresponding microstructure in the medium, which transforms from a homogeneous, isotropic sol into a lattice of polymer waveguides.^{35–37} Transmission optical micrographs of its *yz* and *xy* planes reveal discrete rows of bright spots (corresponding to the transverse cross-sections of waveguides) stacked along *y*; FFT spectra of these images indicate an average inter-row

spacing of 84 μ m \pm 25 μ m (Fig. 2.3k, l, n, o; Fig. 2.10a, b; see 2.10.2 for procedure); this is commensurate with the dimensions of the lattice of filaments in Fig. 2.3d, i. The micrograph of the top-most *xz* plane (Fig. 2.3m) – which cannot be imaged by a CCD camera during lattice formation (Fig. 2.1) - reveals a grid of intersecting waveguides with square symmetry and average periodicity of 86 μ m (Fig. 2.3p; Fig. 2.10c; see 2.10.2 for procedure). This top-down view provides direct evidence that orthogonally propagating filaments spontaneously converge into grids with square symmetry.



Figure 2.3 Simultaneous modulation instability (MI) of mutually orthogonal Beams X and Z propagating through a photopolymerizable sol. The spatial intensity profile of Beam X was imaged at the sample exit face (represented by red square in (a)) and monitored over time. Profiles acquired (b) before and (c) after MI are presented together with (d) corresponding FFT where the central peak has been removed for clarity. The (e) 3-D beam intensity profile highlights the spatial ordering of self-trapped filaments into rows. Corresponding and equivalent images for Beam Z are presented in (f-j). All scale bars = 200 µm. Transmission optical micrographs of the (k) *yz* (l) *xy* and (m) *xz* faces of the photopolymerized microstructure with (n-p) corresponding FFT where the central peak has been removed for clarity. All scale bars = 500 µm.

Simultaneous MI of three mutually orthogonal incandescent beams: a simple cubic lattice of filaments

The filaments self-organize into a 3-D lattice with simple cubic symmetry when Beams X, Y and Z simultaneously undergo MI and generate three mutually orthogonal populations (Fig. 2.4). The spontaneous emergence of the highly ordered 3-D lattice from three mutually incoherent optical fields superposed in a homogenous fluid is an arresting phenomenon. This process is directly observed in real-time by monitoring the evolution of beam intensity profiles (Fig. 2.4a-j) and subsequently, in micrographs of the photopolymerized structure (Fig. 2.4k-p). Consistent with cubic symmetry, filaments at the exit face of Beam X (the (100) lattice plane) exhibit square symmetry, further confirmed by the square symmetry (*i.e.*, reciprocal lattice) of the corresponding FFT spectrum, which yields an average periodicity of 141 μ m ± 32 μ m (Fig. 2.4c, d; see 2.10.2). Square symmetry is also observed in the (001) face (Beam Z exit face) with an average periodicity of 137 μ m ± 43 μ m (Fig. 2.4h, i; see 2.10.2 for procedure). Micrographs of the polymerized structure reveal a cubic waveguide lattice with equivalent (100), (001) and (010) planes that each possess square symmetry (Fig. 2.4km). For e.g., the (010) face (Fig. 2.4m) is a square array (periodicity = 93 μ m ± 26 μ m) of waveguides propagating along the y axis in parallel to the microscope axis. Some of these waveguides capture and guide the white probe beam of the microscope and therefore appear as particularly bright spots (encircled in red). The micrograph also contains the longitudinal profiles of waveguides oriented along the x and z axes, respectively; a magnified inset shows that each lattice point is the intersection of three mutually orthogonal waveguides propagating along x, y and z, respectively. The average periodicity

of the waveguide lattice observed in the micrographs is 93 μ m ± 21 μ m. This value is commensurate with the periodicity observed in the square lattices generated by their parent filaments (*vide supra*, Fig. 2.4c, d, h, i).



Figure 2.4 Simultaneous modulation instability (MI) of mutually orthogonal Beams X, Y and Z propagating through a photopolymerizable sol. The spatial intensity profile of Beam X was imaged at the sample exit face (represented by red square in (a)) and monitored over time. Profiles acquired (b) before and (c) after MI are presented together with (d) corresponding FFT where the central peak has been removed for clarity. The (e) 3-D beam intensity profile highlights the spatial ordering of self-trapped filaments into a square array. Corresponding and equivalent images for Beam Z are presented in (f-j). All scale bars = 200 µm. Transmission optical micrographs of the (k) (100) (1) (010) and (m) (001) planes of the photopolymerized cubic microstructure (n-p) corresponding FFT where the central peak has been removed for clarity. The triple intersection points of filaments propagating along the *x*, *y* and *z* axes (in red dotted circles) All scale bars = 500 µm.

2.5 <u>Mechanism of 3-D self-organization: cooperative, collision-driven interactions</u> of mutually incoherent filaments

We reason and provide additional experimental proof that self-organization of this large population of nonlinear incoherent waves is driven by their dynamic interactions and in particular, preferential collisions with orthogonal neighbours. We consider first the interactions of an *isolated* pair of parallel-propagating filaments during the early, nascent stages of self-organization. Because they are mutually incoherent, *i.e.*, possess extremely poor correlation of phase and amplitude, any overlap of their optical fields always results in superposition and thereby an average increase in intensity. (By contrast, mutually coherent – phase correlated - filaments would suffer constructive (greater intensity increase) or destructive interference (extinction of intensity), respectively.³⁸) The intensity increase leads in turn to an increase of Δn , which triggers the flow of light from both filaments to this interstitial region. As a result, the individual pair of filaments appears to attract and spontaneously shift towards each other and even fuse.^{39,40} In the case of a large population of parallel filaments however, the multiple pairwise interactions of each constituent filament – which is surrounded in all directions by equivalent neighbours – effectively cancel each other out, stabilizing the population and leading to the characteristic inter-filament separation of 110 μ m \pm 33 μ m observed in experiments (Fig. 2.2c, h; see 2.10.2 for procedure).



Figure 2.5 Mechanism of 3-D self-organization of filaments. Schemes of three types of orthogonal interactions between a pair of filaments in (a) a nascent lattice formed by simultaneous MI of Beams X and Z: the filament pair forms (b) at the same height with maximum overlap or (c) with height differences comparable to filament widths resulting in partial intensity overlap or (d) at different heights with negligible intensity overlap. A filament along *y* would cause (e) triple collision with significant overlap (insets) of all three filaments. Evidence of the spontaneous migration of filaments to maximize intersections: (f) evolution of filament positions along a column and row, respectively of an emerging cubic lattice face (INSET) quantified through (g) temporal plots of the standard deviation of filament positions at a given time from their final positions in the row and column, respectively.

The increased Δn in their interstitial regions also governs the interactions of an isolated pair of *orthogonal* filaments (*i.e.*, propagating along x and z). We consider the three types of interactions that are possible in this case (Figure 2.5): in the first, the orthogonal pair of filaments serendipitously form at the same height (v); when they collide, there is complete overlap of optical fields at the volume of intersection with a maximum possible increase in intensity and Δn (Fig. 2.5b). In the second case, filaments are separated in height (along y) by distances comparable to their individual widths; the resulting, *partial* overlap of fields generates a Δn that is sufficiently large to attract light from both filaments, which then spontaneously shift towards (and are attracted to) each other along y until they occupy the same xz plane (Fig. 2.5c). Collision between these filaments now results in the maximum overlap of their optical fields. (Similar deviations of a self-trapped beam in the presence of a perpendicular counterpart have been observed in liquid crystals⁴¹ and theoretically proposed in photoisomerizable polymers.^{42,43}) In the third case, the filaments are separated by such large distances (>> individual widths) that the overlap of their optical fields is negligible and they pass by each other without colliding (Fig. 2.5d). In the first two cases, filaments collide but do not fuse: instead, they intersect without changing trajectories or intensity profiles.²⁶ This soliton-like behaviour is characteristic of self-trapped beams separated by angles exceeding their critical waveguiding angle.⁴⁴ which prevents them from fusing by cross-coupling into each other's waveguides.

The pairwise interactions of individual filaments and in particular, their propensity to maximize the number of collisions with orthogonal counterparts emerge as critical

parameters of self-organization. To enable each constituent filament to balance its attractive interactions with parallel neighbours and maximize collisions with orthogonal ones, the two populations of filaments collectively equilibrate into a stack of 2-D *xz* grids (Fig. 2.3m). This configuration allows the maximum number of intersections between filaments propagating along *x* and *z*, which in turn define the lattice points and square symmetry of the 2-D lattices. The average periodicity of the 2-D lattices of 86 µm (Fig. 2.3m, p) is determined by the optimum distance that balances the attractive interactions between parallel filaments within the grid. Accordingly, it is commensurate with the average separation distance between randomly positioned filaments ($110 \pm 33 \mu m$) generated through MI of a *single* beam (Fig. 2.2). The stability of the stack of 2-D grids along the *y* axis must arise from similar considerations of attractive interactions of coplanar filaments with their counterparts in the nearest (upper and lower) planes and accounts for the average interplanar separation distance of 69 µm (Fig. 2.3d, i).

Although the xz planes containing the 2-D filament grids described above are periodically stacked along the y axis, the corresponding FFT confirms that there is no spatial correlation between individual filaments occupying *different* xz planes, *i.e.*, there is no periodicity along the x or z axes (Fig. 2.3d, i). This changes dramatically when a third filament population is introduced along y and the system spontaneously converges to a simple cubic lattice with periodicity along all three axes (Fig. 2.4). This result can be understood by again considering the parallel and orthogonal interactions of filaments (Scheme 2.1).



Scheme 2.1 Proposed mechanism of self-organization: the MI of Beam Z generates randomly distributed filaments (grey lines). The filaments spontaneously migrate to intersect (red dots) with orthogonal counterparts during the simultaneous MI of Beams Z and X to form 2-D square arrays. Simultaneous MI of Beams Z, X and Y, filaments collectively migrate to maximize triple intersections (red dots), which results in a cubic lattice.

In the case of two orthogonal populations (generated from Beams X and Z), filaments maximize the number of collisions by forming planar xz grids; each lattice point of these 2-D square grids is an intersection of an orthogonal pair of x and z filaments. In the case of three filament populations generated through the simultaneous MI of Beams X, Z and Y, each constituent filament seeks to now maximize collisions with *two* mutually orthogonal counterparts. To achieve this, filaments propagating along the x axis selforganize into stacks of 2-D lattices in *both* the xy and xz planes, filaments along the y axis form 2-D lattices in the yx and yz planes and filaments along the z axis form 2-D lattices in the xy, xz and yz planes – this results in a cubic lattice where each lattice point is a triple collision of three mutually orthogonal filaments propagating along the x, y and z axes.

2.6 Spontaneous migration of filaments

The self-organization of filaments relies on their dynamic and reciprocal interactions and their physical shifting in space (in the directions perpendicular to their propagation axis) in order to maximize collisions with orthogonal neighbours. The real-time shifting of filaments during lattice formation is shown in Figure 2.5f and g, which traces the positions of a row and separately, a column of filaments in the (100) plane. To quantify this behaviour, we plotted the average standard deviation (σ) of an individual filament's position in space with respect to the best-fit line through the positions of all filaments along a row (or column) (see 2.10.5 for procedure). There is a significant decrease in σ observed in both cases ($\Delta \sigma = 17 \ \mu m$ and 16 μm , respectively) compared to the average periodicity of the (100) face (141 $\mu m \pm 32 \ \mu m$; see 2.10.2 for procedure). This signifies that filaments spontaneously move from relatively poorly correlated positions at early times to strongly aligned positions in the final stable lattice.

The shifting of filaments – which in effect are polymer cylinders – must involve the transfer of unsaturated moieties (e.g. monomers, oligomeric chains) from relatively dark areas in the medium to the regions of greater intensity – such as those generated at the intersections of filaments. During the early, nascent stages of polymerization, the smaller viscosities of the still-fluid medium facilitates this migration. For example, the spontaneous migration of low molecular-weight chains has been inferred from previous studies of the interactions of incandescent self-trapped beams³⁹; mass transport of unsaturated moieties to regions of greater intensity has also been observed during the formation of holographic gratings in photopolymerizable thin films.^{45,46} In both cases,

there is a greater depletion rate of unsaturated moieties in regions of greater optical intensity, which generates a gradient in the concentration of unsaturated moieties. This drives the flow of unsaturated moieties in darker areas towards brighter (more polymerized) regions.

The self-organization of filaments relies both on the concentration gradients of unsaturated, polymerizable moieties as well as gradients in optical intensity. These are strongly interdependent parameters: because they undergo greater extents of polymerization, brighter regions in the medium necessarily possess a greater Δn and attract additional flow of intensity, which in turn increases polymerization rates. This nonlinear, reciprocal process drives the collective shifting of filaments in order to maximize the number of simultaneous collisions of three orthogonal (*x*, *y*, *z*) filaments. At these triple collision points - which define the lattice points of the cubic structure – there is complete overlap of the optical fields of filaments and thereby, the maximum possible intensity and Δn (Fig. 2.4e).

2.7 <u>Self-organization of three filament populations into a centred rectangular</u> <u>lattice</u>

To further test the proposed mechanism, we changed the configuration of the three filament populations. We reasoned that a collision-driven process should still elicit self-organization but into a lattice with a different (non-cubic) symmetry. The three incandescent beams were now launched at -45° , 0° and 45° relative to the normal of the *xy* face of the sample. Upon refraction at the air-sample interface, they propagate at $\sim -30^\circ$, 0° and 30° in the medium and simultaneously undergo MI to form three filament

populations (Figure 2.6a-e). Distinct from the case of three mutually orthogonal populations (Fig. 2.4), the propagation axes of filaments in the current configuration contain only *x* and *z* components. Because their intersections are necessarily constrained to *xz* planes, the filaments self-organize into a stack of 2-D lattices with centred rectangular symmetry that are stacked along *y* with a periodicity of 100 μ m (Fig. 2.6c, e, f). The four outmost (red) points of the lattice unit cell are defined by triple collisions of filaments oriented along -30°, 0°, 30° while its central point corresponds to the double collision of filaments oriented along -30° and 30° (Fig. 2.6g). This structure allows the maximum number of triple collisions between these three populations of filaments and is also stabilized by double collisions.



Figure 2.6 Simultaneous modulation instability (MI) of three incandescent beams launched at (a) -45°, 0° (Beam X), -45° with respect to the surface normal of the *yz* face of the photopolymerizable sample. The spatial intensity profile of Beam X was imaged at the sample exit face (represented by red square in (a)) and monitored over time. Profiles acquired (b) before and (c) after MI are presented together with (d) corresponding FFT where the central peak has been removed for clarity. The (e) 3-D beam intensity profile highlights the spatial ordering of self-trapped filaments into rows. All scale bars = 200 µm. Transmission optical micrographs of planes corresponding to the (f) *yz* and (g) *xz* faces of the photopolymerized structure. Dotted red lines in (g) denote the relative propagation axes of the three beams in the sample. The solid red square corresponds to the inset, in which the unit cells of the rectangular centred lattice are indicated for clarity. Here, red and green dots correspond to intersections formed through triple and double collisions, respectively. All scale bars = 500 µm.
We found that highly ordered lattices spontaneously emerge from a spatially and temporally incoherent – chaotic – optical field. To the best of our knowledge, these are the first examples of self-organized 2-D and 3-D ordered microstructures in a weakly correlated system. Lattice formation in this system occurs in the nonlinear regime where MI-induced collapse of broad beams yields large populations of identical filaments. These filaments collectively self-organize because of their soliton-like propensity to intersect and in this way, maximize optical intensity and Δn at their points of intersection. Our findings open a facile pathway that marries the elegant spontaneity of self-organization to the precision of optical lithography to generate highly ordered polymer architectures. Requiring only inexpensive incoherent sources such as incandescent lamps and LEDs and isotropic photopolymerizable sols, this method could allow self-organization of all the Bravais lattices by varying the number of beams and their relative propagation axes in the sample. This is experimentally challenging to achieve through approaches such as chemical self-assembly⁴⁷ and interference-based lithography.⁴⁸ This study presents an accessible platform where the precisely controllable properties of optical fields such as propagation axis, intensity, wavelength and coherence can be employed to stage and study the dynamics of nonlinear pattern formation in incoherent systems. This is especially relevant to naturally occurring self-organizing systems, which subject to random thermal fluctuations, must necessarily comprise poorly correlated waves. The emergence of ordered lattices in an incoherent field also raises fundamentally new questions about entropic changes underlying this transition²⁸ as well as the impact of long-range order on the coherence of the constituent optical fields.

Interestingly, these results appear counterintuitive in the context of optical interference; from the classic experiment of Young in 1804⁴⁹ to holographic lithography developed in 2000⁴⁸, optical lattices have been generated with light beams that possess strong correlations of phase and amplitude. Albeit through an entirely different mechanism, the 3-D cubic lattice in our experiment forms under exactly the *opposite conditions*: when three uniform incandescent beams with spectral ranges comprising all of the visible wavelengths – and which are inherently and mutually incoherent – coincide within an isotropic photopolymerizable sol. Fundamentally different to interference, the *mutual incoherence* of the optical fields is critical here: when these poorly correlated waves are superposed at intersection points, there is always an overall, average increase in intensity. The symmetry of the self-organized lattice corresponds to the real-space positions of intersection points whereas its periodicity is set through a balance of the competing attractive interactions of parallel-propagating filaments.

2.8 Acknowledgements

We thank Hao Lin and Shaochang Song for their contributions to experiments presented in Figure 2.6. We acknowledge the participation of Oskar Niburski in preliminary experiments. We are grateful to Prof. I. Vargas Baca, Prof. J. S. Preston and Prof. M. A. Brook for valuable discussions. Funding from the Natural Sciences and Engineering Research Council, Canadian Foundation for Innovation, Ontario Institute of Technology and McMaster University is gratefully acknowledged. We thank CIBA GEIGY, Canada for generous donation of photoinitiator, IRGACURE-784[®].

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2.9 <u>Supporting information</u>

2.9.1 Methods and materials

2.9.1.1 Preparation of photopolymerizable organosiloxane sols

Sols were prepared through the acid catalyzed hydrolysis and condensation of 3-(trimethoxysilyl)propyl methacrylate (0.071 mol (17.6 g), Sigma Aldrich, ON, CANADA), which was mixed with 1.1 g of 0.05 M HCl; the mixture was stirred vigorously for 10 mins until it homogenized. The clear sol was sensitized to visible wavelengths ($\lambda_{max} = 460$ nm) through addition of 1.8 x 10⁻⁴ mol (0.096 g) of bis(η 5cyclopentandienyl) bis(2,6-difluoro-3-(1H-pyrrol-yl)-phenyl) titanium(IV) (IRGACURE-784[®], Ciba Specialty Chemicals Inc.) and stirred in the dark for at least 16 hrs. The sol, which was transparent and orange in colour, was stored in the dark and filtered through a polytetrafluoroethylene (PTFE) membrane with pore size = 0.2 µm (Pall Corporation, ON, Canada) prior to use.

2.9.1.2 Optical assembly

The custom-built assembly (Fig. 2.1) consisted of three quartz-tungsten-halogen (QTH) lamps (370 nm to 1000 nm) (Cole-Parmer, IL, USA), which were positioned mutually perpendicularly to each other. Each of the three beams X, Y and Z (labelled according to their propagation axis) was collimated through a plano-convex lens (FL_x, FL_y , $FL_z = 250$ mm) before being launched into the sol, which was contained in an optically transparent (10 mm x 10 mm x 10 mm) glass cell (Labomed, inc., CA, USA) sealed with a glass cover slip. The spatial intensity profiles of Beams X and Z at their respective exit faces were each imaged through a pair of plano-convex lenses (FL = 250

mm) onto a high resolution CCD camera (WinCamDTM-UHR models, DataRay Inc., CA, USA). Optical intensities were measured with a power meter (LabMax-TO, Coherent, CA, USA) with a Si sensor (\emptyset = 7.9mm, LM-2 VIS, Coherent, CA, USA). Typical intensities yielding self-organized structures with optimal long-range order were 7.1 mWcm⁻² for experiments with one beam, 4.1 mWcm⁻² for experiments with two beams and 2.0 mWcm⁻² to 2.4 mWcm⁻² for experiments with three beams; approximately the same intensity was employed for each beam in multi-beam experiments. Repeat experiments were conducted to confirm the reproducibility of our observations: 13 experiments for single beam experiments, 13 experiments for two beam experiments and 45 experiments for three beam experiments.

For experiments involving non-perpendicular beams (Fig. 2.6), three QTH lamps were positioned with at -45°, 0°, 45° with respect to the x axis (Fig. 2.6). Each beam was collimated through a plano-convex lens (FL = 250 mm) before entry into the sample. The spatial intensity profile of the beam propagating at 0° at a propagation distance = 6 mm was monitored. Incident intensities employed ranged from 0.6 mWcm⁻² to 1 mWcm⁻² for each individual beam. Five experiments were conducted to confirm reproducibility of results.

In all experiments, we define steady state in filament self-organization as being achieved when there are no longer any significant changes in the spatial positions of filaments; however, at long times, these immobile filaments may undergo a decrease in intensity due to material degradation or phase separation in the polymerizable medium. When generating spatial intensity profiles for movies, we select a relative intensity colour

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scale (red (max. intensity) to blue (min. intensity)) that provides the best signal to noise ratio for the filament populations until steady state has achieved.

2.9.2 Acquisition and analysis of FFT spectra

Spatial intensity profiles for Fast Fourier transform were digitized into a 2-D matrix (126 x 126) containing values of intensity. To remove background signal, the minimum intensity value was subtracted from all elements of the matrix. The Fourier function in the Mathematica software suite was then applied to each element:

Fourier[data, FourierParameters \rightarrow {1, 1}]

The absolute values of the real part of the transform were collected and the minimum value from the transform was subtracted from each value to reduce noise. In order to improve the signal of the higher frequency peaks, the peak at zero frequency was set to zero.



Figure 2.7 (a) The spatial intensity profile of the *yz* plane (corresponding to the output face of Beam X) resulting from simultaneous MI of Beams X, Y and Z and corresponding 2-D FFT before (a) and (b) after subtraction of zero frequency peak. Each 2D FFT image is normalized to the peak with the greatest intensity.

Horizontal and vertical 1-D cross-sections of FFT spectra corresponding to spatial intensity profiles were analyzed (see Figure 2.7). The existence of periodicities in a profile was indicated by peaks with significant magnitudes compared to a profile containing only randomly distributed filaments. Periodicities were determined by taking the inverse of the frequencies of peaks with the greatest magnitude. Although multiple harmonic peaks with significant magnitudes were detected in the same 1-D profiles, they all originate from the same periodicity. Minor deviations from the harmonic frequencies could be attributed to local variations in separation distances or intensities between filament rows. To further ensure the validity of periodicities acquired from FFT, we cross-checked and confirmed that they were commensurate with values that were manually calculated from the spatial intensity profiles (Table 2.1 and 2.2).



Figure 2.8 Spatial intensity profiles and corresponding FFT of the *yz* plane (output face of Beam X) for MI of (a) Beam X and simultaneous MI of (b) Beams X and Z and (c) Beams X, Y and Z. 1-D profiles of the vertical (blue) and horizontal (red) cross-sections of the FFT spectra were analyzed using the peaks with the greatest intensities (indicated by dotted lines).

2.9.3 Determination of the spatial coordinates of filaments and manual measurements of

separation distances and periodicities

The spatial coordinates (xy) of filaments were determined through a Python program,

which defined filament centres as local maxima with intensities > 50 % of the maximum

intensity in the spatial intensity profile. The average separation distance in a randomly

distributed population of filaments was determined by taking measurements between 100

pairs of neighbouring filaments. Values were converted from pixels to micrometres based

on the CCD resolution (9.30 μ m pixel⁻¹ or 10.40 μ m pixel⁻¹). The position of horizontal rows (or vertical columns) of filaments were defined by the average position along the *x* axis (or *y* axis) of filaments along the line with an associated standard deviation. Separation distances (including periodicity) were determined by averaging the differences in positions of 8 to 14 neighbouring lines (Figure 2.9).



Figure 2.9 Scheme of procedure employed to measure distances between filaments.

2.9.4 FFT of optical micrographs of polymer microstructures

2.9.4.1 Simultaneous MI of Beams X and Z: stack of 2-D square arrays



Figure 2.10 2-D FFT of micrographs of polymerized microstructure resulting from the simultaneous MI of Beams X and Z. Images correspond to the (a) yz, (b) xy and (c) xz (c) planes. 1-D profiles of the vertical (blue) and horizontal (red) cross-sections of the FFT spectra were analyzed using the peaks with the greatest intensities (indicated by dotted lines).



2.9.4.2 Simultaneous MI of Beams X, Y and Z: cubic array

Figure 2.11 2-D FFT of micrographs of polymerized microstructure resulting from the simultaneous MI of Beams X, Y and Z. Images correspond to the (a) *yz*, (b) *xy* and (c) *xz* (c) planes. 1-D profiles of the vertical (blue) and horizontal (red) cross-sections of the FFT spectra were analyzed using the peaks with the greatest intensities (indicated by dotted lines).

Metho d	FFT of spatial intensity profiles Face				Manu	al	FFT of corresponding microstructure		
					Face	2	Face		
	yz	xy	XZ	yz	xy	XZ	yz	xy	XZ
Vertical direction (µm)	69	69		69 ± 6	74 ± 10		66	2 10	86
Horizont al direction (µm)									86

Table 2.1 Measurements of periodicity of rows and columns of filaments in a stack of 2	2-
D square arrays generated through simultaneous MI of Beams X and Z.	



Table 2.2 Measurements of periodicity of rows and columns of filaments in a 3-D cubic lattice generated through simultaneous MI of Beams X, Y and Z.

Metho d	FFT of spatial intensity profiles				Manu	al	cor mic	FFT of corresponding microstructure				
		Face			Face			Face				
		yz	λ	y	XZ	yz	xy	XZ	yz	xy	XZ	,
Vertical		11	1	0		10	10		86	11	12	
direction	9		7			3 ± 16	7 ± 17			2	4	
(µm)												
Horizont		16	1	6		15	10		70	74	93)
al direction	4		7			2 ± 29	5 ± 26					
(µm)												



Table 2.3 Measurements of inter-filament spacing within lines (as outlined in Figure 2.5	8)
for the 2 and 3 beam experiments.	

Experiment	Simul	taneous MI X and Z	of Beams	Simultaneous MI of Beams X, Y, and Z					
		Face		Face					
	yz	xy	XZ		уz	xy	XZ		
Vertical					$103 \pm$	121 ±	:		
direction (µm)				31		37			
Horiztonal	74 ±	69 ±			$155 \pm$	105 ±	:		
direction (µm)	26	26		44		50			

2.9.5 <u>The spontaneous migration of filaments</u>

To trace the migration of filaments during self-organization, the standard deviation of the average position of filaments along a horizontal row or vertical column in the lattice was plotted over time.



Figure 2.12 Temporal evolution of a horizontal row of filaments. Black dots represent the local maxima of each filament along the row; white dotted lines correspond to their their average position on the *y*-axis at a given point in time.

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3 <u>A soft photoresponsive material that computes with</u> <u>filaments of white light[†]</u>

3.1 Abstract

Next-generation stimuli-responsive materials must be configured with local computational ability so that instead of a discrete on-off responsiveness, they sense, process and interact reciprocally with environmental stimuli. Towards this objective, we present a photopolymer cuboid that autonomously performs pattern recognition and transfer, volumetric encoding and binary arithmetic with incandescent beams. The material's nonlinear response to incident beams generates one, two or three mutually orthogonal ensembles of white-light filaments, which respectively self-organize into disordered, 1-D and 2-D periodic geometries. Data input as binary (dark-bright) strings generate a unique distribution of filament geometries, which corresponds to the result of a specific operation. The working principles of this material that computes with light is transferrable to other nonlinear systems and incoherent visible light sources including light emitting diodes.

[†] Manuscript (adapted) submitted to Nature Communications on July 9th, 2018. The authors of this manuscript are Alexander D. Hudson, Matthew R. Ponte, Fariha Mahmood, Thomas Pena Ventura, and Kalaichelvi Saravanamuttu. Contribution: Hudson and Ponte equally contributed to this work. Hudson, Ponte, Mahmood, and Saravanamuttu were responsible for writing the manuscript. Hudson and Ponte were responsible for designing the experiments, running the $2^2 X 2^2$ experiments, and performing the FFT analysis. Hudson and Ventura were responsible for designing and running the encoding experiments, and analyzing the results. Hudson and Mahmood were responsible for designing and running the arithmetic experiments.

3.2 Introduction

Soft polymer thin films, monolayers, colloids, fluids, gels and solids are essential for the design of stimuli-responsive systems and devices 1^{-3} . When stimulated by electromagnetic, electrical, chemical or mechanical signals, these pliant polymer architectures transition between states while exhibiting discrete changes in physical or chemical properties that can be harnessed for biosensing⁴, controlled drug delivery⁵, tuning photonic band gaps^{6,7}, surface wettability and swelling⁸. The ultimate objective of this field is the biomimicry of intelligent responsiveness such as tactility, vision, camouflage, contractility and flight where complex natural sensors such as skin, eye and muscle seamlessly adapt to environmental stimuli through exquisitely programmed response-sequences⁹. Artificial intelligent sensing systems could be developed by configuring local computational ability into soft polymer constructs and in this way, enabling autonomous sensing, manipulation and processing of stimuli signals without the need for external processors or electrical power. A recent and seminal example of such a "material that computes" coupled the nonlinear self-oscillations generated through the Belouzov-Zhabotinsky reaction in a group of gels with piezoelectric (PZ) cantilevers to perform binary pattern recognition¹⁰.

Here, we present a self-contained, soft photoresponsive system – comprising only a homogeneous photopolymerizable fluid contained in a transparent cuboid and up to three beams of white incandescent light – that performs multiple operations including the recognition and transfer of binary data, single-step volumetric encoding and two foundational operations of digital computing - the addition and subtraction of binary

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strings (Figure 3.1). These operations are performed by large ensembles of nonlinear optical waves, specifically soliton-like filaments, which originate from the nonlinear response of a photopolymerizing medium to incident optical fields^{11–13}. Binary data input into the cuboid as black and bright stripes of light precisely control the 3-D spatial distribution and self-organization of filaments and in this way, generate the result of an operation, which can be read in a single step at the cuboid output face. Because it is based on nonlinear waves, which are unified through mathematical expression and exhibit strikingly similar dynamics in disparate media ¹⁴, this system provides proof of a concept that is transferrable to a wide range of nonlinear materials with photoresponses that can be tuned in terms of reversibility, speed and magnitude^{15,16}. Equally powerfully, the system functions with low energy, incoherent white light – like sunlight - comprising all visible wavelengths and is therefore also operable with compact, inexpensive and visible light emitting diodes (LEDs), which typically emit incoherent light.

3.3 **Results and Discussion**

Figure 3.1 depict the working principles of our system, which consists of dense populations (~8000 cm⁻²)¹¹ of white light filaments confined to a polymer cuboid (~1 cm³). Up to three mutually orthogonal populations of filaments are generated through the modulation instability (MI) – stochastically driven filamentation^{11,12,15,17,18} – of broad incandescent beams ($\Delta\lambda$ = 370 nm to 1000 nm) launched along the *x*, *y* and *z* axes of the cuboid, which originally contains a photopolymerizable organosiloxane fluid^{11,13,19,20}. Mechanisms underlying the MI of optical fields in this and other polymerizable systems have been detailed elsewhere^{17,18,21,22}. Briefly, when launched into the cuboid, a broad

incandescent beam with a uniform spatial intensity profile initiates free-radical polymerization along its propagation axis. Corresponding refractive index changes (Δn) push the nascent system into the nonlinear regime where noise – normally insignificant and random intensity variations - becomes amplified. As intensity modulations grow, the beam becomes unstable and collapses into large populations of statistically equivalent filaments. Each filament induces a high-refractive index channel along its path, populates this cylindrical waveguide as bound modes and travels through the medium without diverging. Two properties of MI-induced filaments are critical to our system: akin to spatial solitons, the filaments are discrete, non-divergent beams that form only under nonlinear conditions. Under linear conditions by contrast, they would blur and rapidly become indistinguishable from each other due to the significant natural divergence of incandescent light. Secondly, because they originate from spatially and temporally incoherent light^{11–13,15,17–19,21,22}, the filaments do not suffer optical interference despite their close proximity. Such dense populations of non-interfering discrete filaments is extremely challenging to achieve with coherent laser light.

The operations performed by this system are based on four distinct types of spatial ordering, which originate from the collective interactions and spontaneous self-organization of filament populations¹³ (Fig. 3.1A): because they are seeded by noise, filaments generated through MI of a single, broad beam are randomly distributed in space and appear at the cuboid exit face as a disordered population of high-intensity spots, which we represent as **0D**. Two mutually orthogonal filament populations – generated through simultaneous MI of two beams – spontaneously organize into a periodic stack of

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grids, which appear as rows of spots at the output. Depending on the propagation axes of the beams, rows are periodically stacked along the horizontal or vertical directions and denoted **1DH** and **1DV**, respectively. Three mutually orthogonal populations, generated through simultaneous MI of three beams, self-organize into a cubic lattice; the output in this case, is a square array of spots **(2D)**.

For the operations, we designate the filament population propagating along x as *carriers*, which are operated on by their orthogonal counterparts – *encoders* - travelling along y and z. Data are input by patterning the beams launched along y and z with a binary sequence (string) of bright and dark stripes (bits). Because MI-induced generation of encoders occurs exclusively in the bright bits, the input of binary strings effectively divides the polymer cuboid into micro-volumes - voxels - in which carriers encounter 0, 1 or 2 encoder populations and therefore respectively adopt the 0D, 1DH, 1DV or 2D configuration (Fig. 3.1B). The consequent distribution of carrier configurations in the voxels provides the result of an operation, which is output at the exit face (yz plane) of the cuboid as a unique combination of the quaternary configurations.



Figure 3.1 Schemes and actual spatial intensity profiles of (A) disordered (0D), onedimensionally ordered (1DH, 1DV) and two-dimensionally ordered (2D) configurations of carrier filaments at the output face (yz plane) of the polymer cuboid. (B) Simultaneous input of binary strings along the y and z axes divides the cuboid into voxels, each containing a specific configuration of carrier filaments. The inset highlights the output of voxels containing the four possible filament configurations.

The first operation that we demonstrate is the recognition of a string of binary data by the system and its transfer to an orthogonal beam (Fig. 3.2). Here, Beam X has a uniform intensity profile while Beam Z is patterned with the binary string of seven stripes (N = 7)with alternating dark (intensity << threshold for MI) and bright (intensity > threshold for MI) intensity (Fig. 3.2A). When launched into the photopolymerizable medium, the entire Beam X suffers MI and generates carriers propagating along x throughout the cuboid. However, MI of Beam Z and generation of encoders along z are confined to rectangular prismic volumes - voxels - defined by its bright stripes. Carrier filaments travelling along x therefore encounter (and self-organize with) encoders travelling along z only within these voxels; they remain disordered everywhere else (Fig. 3.2B). The output of the carriers (Fig. 3.2C) is a binary sequence of seven stripes with alternating configurations of disordered (0D) and one-dimensionally ordered (1DH) spots. The output is read in a single-step and quantified through FFT analysis, which reveals high frequency peaks only for the ordered 1DH configuration (Fig. 3.2D). The output exactly matches the binary string input through Beam Z where the dark and bright stripes correspond to the 0D and 1DH states, respectively and confirms its transfer to the initially uniform Beam X.



Figure 3.2 Recognition and transfer of a binary string comprising (A) seven dark and bright stripes (bits) launched through Beam Z into the polymer cuboid. The spatial intensity profile of Beam X at the output (*yz*) plane is imaged onto a CCD. The output string consists of seven stripes of (B) alternating 0D and 1DH configurations, which (C) corresponds to the input binary string [Scale bar = $200 \ \mu m$; blue (minimum) to red (maximum) intensity scale provided]. (D) FFT spectra of areas of the output contained in red squares. 1-D vertical and horizontal profiles acquired through the origin are provided in black; for reference, averaged 1-D vertical profiles of the entire spectrum are provided in red.

The system also performs *active* operations – where input data are processed to yield a result - by employing both orthogonal populations of encoders (Fig. 3.3, experimental setup shown in Fig. 3.6). An active operation generates a unique 3-D distribution of carrier configurations within the cuboid; this result is output at the exit face as a specific combination of the quaternary (0D, 1DH, 1DV and 2D) carrier configurations. The first active operation that we demonstrate is the single-step volumetric encoding of optical data in the polymer cuboid. Here, two independent binary strings input through Beams Y and Z, respectively combine within the polymer cuboid and divide it into voxels. All voxels are populated by carriers but contain different numbers (0, 1 or 2) of encoder populations and therefore, different carrier configurations. This is different from conventional 3-D optical data storage, which must employ high-intensity, two photon processes to access volumetric control and writing of binary patterns in the photochromic material is carried out element by element²³. Equally importantly, the read-out in our system is also a single-step, non-destructive process and is based on the output of waveguides. By contrast, conventional techniques typically rely on the luminescence of chromophores for the element-by-element read-out process, which moreover can lead to photobleaching of encoded information.

In the simplest case of encoding (Fig. 3.3A), Beams Y and Z are each patterned with a binary string of one bright and one dark stripe (N = 2) while Beam X remains uniform. MI occurs everywhere in Beam X to form carriers but encoders form only within the bright stripes of Beams Y and Z and divide the cuboid into quadrants or four cubic voxels. In the upper left voxel, carriers encounter encoders only along *z* and assume configuration 1DH while in the lower right voxel, they adopt the 1DV configuration due to equivalent interactions with encoders along *y*. Carriers remain disordered in configuration 0D in the lower left voxel where neither Beam Z nor Beam Y suffers MI. In the upper right voxel, all three filament populations self-organize into a cubic lattice and

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thereby the 2D configuration. At the *yz* output plane, the distinct configurations of the carrier filaments are quantitatively confirmed through FFT analysis (Fig. 3.3A).

To demonstrate the versatility of the encoding operation, we generate and read-out a sequence of alphabet letters that spell "incoherent beam" (Fig. 3.3C). The letters are volumetrically encoded in the cuboid and generated through a specific pair of orthogonal binary strings input through Beams Z and Y. For example, the two binary strings -010and 10001 - operate on carrier filaments to generate the letter "I" within the cuboid (Fig. 3.3B). The two horizontal strokes of the letter are defined by the 1DH configuration, which results from the combination of the "1" bit in Beam Z (which generates encoders along z) and "0" bit in Beam Y (which suppresses MI along y). Conversely, the vertical stroke of "I" corresponds to the 1DV configuration of carriers resulting from the combination of the "1" bit in Beam Y (which generates encoders along v) and "0" bit in Beam Z (which suppresses MI along z). At the intersections of the horizontal and vertical strokes, carriers adopt the 2D configuration due to the combination of "1" bits from both Beams Y and Z (generating encoders along both y and z). The encoded letter can be visualized in real space and through FFT, distinguished from the background 0D configuration (the latter has been dulled in Fig. 3.3B-C as a guide to the eye).



Figure 3.3 Single-step volumetric encoding in the polymer cuboid. Output face (*yz* plane) of polymer cuboid when (A) encoded by two identical binary strings 0 (black bar) 1 (white bar) introduced along the *y* and *z* axes. The four carrier configurations at the output were quantified through FFT analysis of select regions indicated by red squares; (B) when encoded by binary strings 010 and 10001 to generate the letter "I". Carrier configurations are labelled; (C) when encoded with different binary string pairs to generate words "incoherent beam". [In (A) - (C), blue (minimum) to red (maximum) intensity scales are provided; scale bar = 500 µm; in (B) - (C), the 0D configuration has been dulled to guide the eye.]

The quaternary nature of its output increases the capacity of our system by 2^{N} -fold compared to the conventional binary string of electrical bits. Given integral number N = number of bits, an electrical binary string with N = 2 allows 2^{2} = 4 possible combinations,

i.e. 00, 10, 01 and 11. By contrast and as depicted in Fig. 3.4A, two such binary strings can be simultaneously input into our system to generate $2^{N} \times 2^{N} = 2^{4} = 16$ combinations of the quaternary configurations 0D, 1DH, 1DV, 2D. These predicted combinations exactly match experimental results (Fig. 3.4B and Fig. 3.7), which are quantitatively confirmed in corresponding FFT spectra (Fig. 3.4C and Fig. 3.8). The output combination in our system can be read in a single step and quantified (and therefore digitized) through FFT analysis.



Figure 3.4 (A) Expected and corresponding (B) experimental results of the 16 (2^2x2^2) patterns generated at the polymer cuboid output (*yz* plane) by all combinations of a pair of 2-bit binary strings introduced along the *y* and *z* axis. Each output pattern comprises different combinations of carrier configurations 0D (red), 1DH (blue), 1DV (green) and 2D (grey), which can be quantified through (C) corresponding FFT spectra of experimental results. (Bits 0 and 1 are represented by white and black bars, respectively; scale bar in (B) = 200 µm; in (B)-(C), blue (minimum) to red (maximum) intensity scales are provided.)

Most significantly, its quaternary output enables the system to perform two fundamental operations of binary arithmetic – addition and subtraction (Fig. 3.5). The scheme in Fig. 3.5A depicts the addition of two binary strings, 10 and 01, input respectively through Beams Y and Z; in all cases, MI of uniform Beam X generates carriers throughout the cuboid. The place value of the binary strings increases from right to left for Beam Y and from top to bottom for Beam Z. The strings divide the cuboid into voxels, each of which contains 0, 1 or 2 encoder populations that operate on carriers and generate a unique output. The sum in binary form is read from the antidiagonal of the output; each element is the result of the operations of encoders with the same place value on the carriers. To interpret results, we assign a value of 0 to configuration 0D, 1 to 1DH and 1DV and 0 carry 1 (0C1) to 2D. In Fig. 3.5A, the addition of 01 and 10 generates an antidiagonal of two elements comprising the 1DV and 1DH configurations, respectively. This correctly represents a sum of 11. For the addition of 0 1 and 0 1 shown in Fig. 3.5B, the first element of the antidiagonal reads "0C1" and the carried value is read from the off-diagonal as 1. Because the second element of the antidiagonal is 0, the sum is 10. Experimental examples of addition in the $2^2 \times 2^2$ system (Fig. 3.4) are tabulated in Fig. 3.5C and classified according to the absolute value of the sum. Because the addition of different pairs of numbers can have the same sum, the 10 tabulated patterns correspond to 4 unique results. Interestingly, although addition is commutative, our system has the ability to distinguish between the 1DH and 1DV configurations, which both correspond to "1". This allows the identity of the input binary strings to be elucidated from the result.

The system is scalable. For a $2^{N} \times 2^{N}$ system, the maximum computable sum = $2^{N} - 1$. For example, in the $2^{5} \times 2^{5}$ system shown in Fig. 3.5D, the largest possible sum is 31. We use this system to demonstrate the addition of 10010 and 01010 to yield a sum of 11100. Using the same system, we also demonstrate the subtraction of the same numbers (Fig. 3.5E). In the case of the latter, we employ the radix complement method employed in digital computing (details in 1.5.2.2)²⁴.



Figure 3.5 Schemes of addition of (A) 01 + 10 and (B) 01 + 01. Addends are input as binary strings through Beams Y and Z; place values are indicated. The result is contained in the antidiagonal of the output (*yz* plane). Carrier configurations 0D (red spots) = 0, 1DV (green spots), 1DH (blue spots) = 1, 2D (grey spots) = 0C1 (C) Addition is commutative and different addend pairs generate different output patterns but the same sum; examples from the $2^2 \times 2^2$ system are tabulated. Any addend may be added on the grid, provided that the sum does not exceed *N* digits for a $2^N \times 2^N$ grid. Shorter binary strings are accommodated by appending leading zeroes as shown in (D) for the sum of 10010 and 1010 performed on a $2^5 \times 2^5$ system. Subtraction is accomplished by adding the two's complement of the minuend. We determine (E) the difference between 10010 and 1010 by adding 10110 and dropping the leftmost digit. This occurs naturally as the bottom-right voxel signifies a carried digit that cannot be contained within the grid. (in (C)-(E), scale bar = 500 µm)

The system employs a two-step process to perform addition: the two addend binary strings are input simultaneously and the output containing the result including carried digits is read in a single step. This contrasts with digital computing where addition is performed by *adders* consisting of sequences of transistor-based logic gates²⁴. An individual *full-adder* determines the sum of three binary inputs, which typically comprise two addends and a carried value²⁴. *N* full-adders are required to find the sum of two *N*digit numbers. In a typical *carry lookahead* device, pairs of digits with the same place value are first analysed to calculate carried values. The sums at each place-value including any carried values are then determined in parallel²⁴. Both our system and digital computing employ the two's complement method to perform subtraction, enabling the same hardware to be employed for both addition and subtraction operations^{24,25}.

We have shown that a self-contained, single-component, light-responsive system performs sophisticated operations on incident optical fields without relying on external electrical power or processors. The system responds to low intensity, incandescent light that – similar to ambient sunlight – comprises all visible wavelengths and is moreover, spatially and temporally incoherent. Interestingly, this system is reminiscent of the light-guiding-model proposed by Snyder²⁶ more than two decades ago in which the pairwise interactions of spatial solitons propagating through a photoresponsive monolith forms the basis of logic operations. Because of the characteristic universality in dynamics and interactions of nonlinear waves, the working principles of this system is applicable to other nonlinear materials. Moreover, because it operates with incandescent light, the system should be operable at all the visible wavelengths. For example, we already

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showed that the generation the 16 distinct output patterns of the $2^2 \times 2^2$ system with miniature blue LEDs (Fig. 3.9).

3.4 Acknowledgments

We are grateful to Prof. Vargas Baca for valuable discussions. We acknowledge the participation of Mr. Oskar Niburski in preliminary experiments of pattern recognition. We thank the Moran-Mirabel group and the Brockhouse Institute for Materials Research, McMaster for technical assistance. Funding from the Natural Sciences and Engineering Research Council, Canadian Foundation for Innovation and McMaster University is gratefully acknowledged. **Author contributions:** ADH and MRP contributed equally to this work. ADH, MRP, FM and KS conceived experiments, analyzed data and wrote the manuscript. ADH, MRP, FM and TPV performed experimental work.

3.5 <u>Supporting Information</u>

3.5.1 Materials and Methods

3.5.1.1 Preparation of photosensitized organosiloxane sols

The polymerizable material was prepared as previously described by our group^{11,13}. Briefly, 17.6 g (0.071 mol) of 3-methacryloxypropyltrimethoxysilane (MAPTMS, Sigma Aldrich) was hydrolyzed by mixing with 1.1 g of 0.05 M hydrochloric acid (Sigma Aldrich), which lead to a condensation polymerization. The sol was then photosensitized with 0.096 g (1.8 x 10⁻⁴ mol) of bis(η^5 cyclopentandienyl) bis(2,6-difluoro-3-(1H-pyrrol-yl)-phenyl) titanium(IV) (Ciba Specialty Chemicals Inc., $\lambda_{max} = 460$ nm) and left stirring for a minimum of 24 hours. The resulting sol was transparent and orange in colour. It was stored in the dark and filtered through a polytetrafluoroethlyene membrane (Pall Corporation, pore size = $0.2 \mu m$) prior to irradiation.

3.5.1.2 Optical assembly

A custom-built optical assembly (Fig. 3.6A) was used to conduct all experiments. Three mutually incoherent white light sources (quartz-tungsten halogen lamps, Cole Parmer, 370 nm to 1000 nm) were positioned 90 degrees apart with respect to each other. The beams were each collimated using a planoconvex lens (FL = 250 mm) before being launched into the sample. Each beam is characterized as an "encoder" (Beam Y and Z) or a "carrier" (Beam X). The intensity profile of the carrier was imaged using two planoconvex lenses (FL = 250 mm) and a CCD camera (DataRay Inc.) mounted on an optical rail.

3.5.1.3 Optical experiments

Samples were prepared as illustrated by Fig. 3.6B. Glass cells were prepared from cuvettes (10 mm H x 10 mm W x 5 mm L) with glass coverslips glued to the top to create a uniform surface at all faces of the sample. Vinyl masks were designed (Adobe Illustrator CS6) and cut (Graphtec America Inc.) for each desired pattern. The masks were applied to the corresponding faces of the cell and the sol was syringed into the cell via a hole between the coverslip and the cuvette. The cell was irradiated in the optical assembly typically until the spatial positioning of the filaments had achieved a steady state¹³, typically taking 20 minutes. The power of the beams was measured using a power meter with a Si sensor (Coherent). Carrier and encoder beams were set at 0.5 mW and 2.5 mW - 3.0 mW, respectively, to achieve optimal pattern formation.
3.5.2 Supplementary Text

3.5.2.1 Acquisition and analysis of FFT spectra

Spatial intensity profiles of resulting patterns were segmented depending on the operation carried out. For the transfer of a binary string between two beams, the spatial intensity profiles are each divided into equal-sized horizontal stripes, with the number of regions determined by the length of the inputted binary string. For the transfer of binary strings between three beams, the spatial intensity profile of Beam X is divided horizontally and vertically, with the number of segments dependent on the length of the inputted binary string in the corresponding axis.

A square region was taken from each of the segments in the spatial intensity profile and digitized into a 2-D matrix (60 x 60 for two beam encoding, 100 x 100 for three beam encoding) containing the intensity values. Regions were selected where noise from random fluctuations in the material was minimal (Fig. 3.2B, 2.3A and 2.7 shows the regions selected for the two beam encoding and three beam encoding, respectively). The minimum intensity value was subtracted from all elements in the matrix to remove background noise and the Fourier function in the Mathematica software suite was applied to each element, with the corresponding parameters:

Fourier[data, FourierParameters \rightarrow {1,1}]

The absolute values of the transform's real portion were collected. The minimum value of the new matrix was subtracted from each value. The peak at zero frequency was set to zero to resolve the higher frequency peaks.

The central horizontal and vertical 1-D cross-sections of the obtained FFT spectra were obtained and normalized with respect to all spectra within the same experimental subset. A threshold spectrum was determined by averaging the peak intensity of all expected ordered regions (within the corresponding subset) at every frequency. Each 1-D FFT spectrum was compared to the threshold spectrum and the presence of ordering was determined by the appearance of a significant number of peaks above the threshold. Examples of these spectra are shown in Fig. 3.8.

3.5.2.2 Radix complement method

This method was adapted from the two's complement method used to represent signed integers in digital computing^{24,25}. The radix complement of any *N*-digit number *z* in base-*b* is $b^N - a$. In binary or base-2, this is the two's complement. To determine the difference between two positive integers *y* and *z*, (y - z), we first obtain the two's complement of *z*, denoted *z*'. The binary strings *y* and *z* ' are input into the material and the resulting pattern is interpreted as a sum. This sum, (y + z'), is the two's complement of the difference. It can be readily converted to the desired difference by discarding the leftmost (most significant) digit. If this operation is performed on the smallest possible grid (i.e. an N by N grid where N = the number of digits of the largest input value), this leftmost bit naturally overflows the boundaries of the grid and is therefore automatically discarded. For cases where *z* and *y* have a different number of digits, leading zeroes are added to the smaller number, and both are treated as *N*-digit values. This method is applicable for differences $(y - z) \ge 0$, where *y*, $z \ge 0$.



Figure 3.6 Schematic illustrations of the optical assembly and mask configuration for encoding experiments. (A) The optical assembly. Quartz-tungsten halogen (QTH) lamps launch beams of incoherent white light into a sample (S) after passing through a collimating lens (L1). The intensity profile at the exit face of the sample is imaged using a pair of lenses (L2, L3) and a charged-coupled device (CCD) camera. (B) Zoom-in of the sample in the optical assembly. Vinyl masks were placed on the sample cell at the entrance face of each encoder, preferentially blocking light from entering the sample at designated regions. The path length and light intensity differed along the x-axis and the y-and z-axis as to maximize waveguide interactions between the beams.



Figure 3.7 Representation of analysis process for each pattern in the $2^2 \times 2^2$ encoding system. Black lines show the division of quadrants within each intensity profile, while the white square indicates the central pattern. Each red square represents the area used to produce the Fourier transform that was analyzed. [Scale bars = 200 µm]



Figure 3.8 Two-dimensional plots of the central axis in the Fourier transforms of the intensity profiles for the two-panel system. The horizontal axis is represented in (A), (C), and (E) and the vertical axis is represented in (B), (D), and (F). The averaged spectrum for all ordered regions is shown in red for all graphs. (A) and (B) shows the averaged spectrum for all unordered regions in blue, (C) and (D) shows the spectrum for one unordered region in black, and (E) and (F) show the spectrum for one ordered region in black. [Gray dotted lines indicate region of interest due to filament diameter in the spectrum]



Figure 3.9 Intensity profiles (A) and corresponding FT spectra (B) for 16 different patterns in the $2^2 X 2^2$ encoding system using blue LEDs as the light source. [In (A), scale bar = 1000 µm; blue (minimum) to red (maximum) intensity scale provided; in (B), black (minimum) to white (maximum) intensity scale provided]

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4 <u>Single-step generation of flexible, free-standing arrays of</u> <u>multimode cylindrical waveguides[‡]</u>

4.1 Abstract

Polymer matrices patterned with 3-D waveguide circuitry are critical components of flexible photonics but cannot be fabricated through conventional, linear lithographic techniques. By exploiting the spontaneous filamentation and modulation instability (MI) of a uniform optical field in a range of silicone-acrylate based photopolymerizable fluids, we report the generation of free-standing arrays of cylindrical, multimode waveguides with tunable flexibility in a single, room-temperature step. A broad, incandescent beam becomes unstable and spontaneously divides into a large population (~10,000 cm⁻²) of microscopic filaments; each filament becomes entrapped within a self-induced cylindrical waveguide and propagates through the medium without diverging. By spatially modulating the beam, it is possible to generate cylindrical waveguide arrays with square symmetry. By controlling the extent of cross-linking and the relative amount of silicone surfactant in the polymerized matrix, it is possible to tune the hardness of the arrays over an order of magnitude (Shore-OO 9 ± 5.0 to 94 ± 2). We show that flexible waveguide arrays that possess relatively low values of hardness can be reversibly compressed to up

[‡] Manuscript (adapted) submitted to Advanced Engineering Materials on August 15th, 2018. The authors of the manuscript are Alexander D. Hudson, Czerysh Bacus, Marlena Whinton, Michael A. Brook, and Kalaichelvi Saravanamuttu. Contribution: Hudson, Brook and Saravanmuttu were responsible for writing the manuscript. Hudson, Bacus, and Whinton were responsible developing the composition of the polymer system. Hudson was responsible for running the optical experiments, performing the compression measurements, and analyzing the results.

to 70 % of their original lattice parameter while retaining waveguiding capacity; the arrays exhibit 100 % recovery after multiple cycles of compression and decompression.

4.2 Introduction

Stimulated by recent advances in stretchable electronics,^{1–3} considerable effort has been devoted to developing flexible photonics systems and optical devices.^{4–7} Such constructs are typically embedded within flexible polymer films, which retain optical functionality during compression or deformation.^{6,8,9} Examples range from plasmonic antennae for signal enhancement^{10,11} to silicon-based photonics circuits.^{12,13} Channel waveguides are fundamental components of photonics and serve as efficient conduits of light signals in integrated-optics. To be viable and ultimately match the density and capacity of microelectronics systems, flexible photonics devices require dense, 3-D waveguide circuitry, which confine and transmit optical signals even upon deformation. Such architectures cannot be generated with conventional lithographic techniques.

Towards this objective, we describe a single-step, room temperature technique to generate flexible polymer films embedded with dense, periodic arrays of cylindrical, multimode waveguides. To achieve this, we exploit the modulation instability (MI) of an incandescent beam as it propagates through a nascent, free-radical polymerization system. Refractive index changes associated with polymerization generate the conditions necessary to elicit nonlinear waveforms of even the spatially and temporally incoherent wavepacket of incandescent light.^{14–16} In this nonlinear regime, a uniform incandescent beam suffers MI-induced division into an ensemble of self-trapped filaments that propagate through the medium without diverging through self-induced cylindrical

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multimode waveguides.^{14,17,18} As a consequence, polymer matrices can be volumetrically patterned with waveguide populations, which efficiently guide broad ranges of visible light even under passive conditions.^{19–23} Organosiloxane-based photopolymers that we predominantly employed in previous studies are rigid, hard materials (Shore-OO hardness value > 95), which are moreover susceptible to cracking and degradation over time.^{20,21,24} We now show that MI of incandescent light can be successfully elicited in a family of silicone-acrylate composites to generate free-standing arrays of cylindrical, multimode polymer waveguides. Significantly, by varying the composition and tuning the extent of cross-linking in the polymer matrix, it is possible to vary the flexibility of the waveguide arrays over an order of magnitude.

4.3 <u>Results and Discussion</u>

4.3.1 Modulation instability of white light

Flexible waveguide arrays were generated in a photopolymerizable solution consisting of varying amounts of 2-hydroxyethyl methacrylate (HEMA), diethylene glycol diacrylate (DEGDA) and a polymerizable silicone surfactant (Silmer ACR A008-UP) (Scheme 4.1); the mixture was sensitized to the blue-green region of the visible spectrum through the addition of 0.5 wt. % of a titanocene free-radical photoinitiator Irgacure 784[®] ($\lambda_{max} = 463$ nm).



Scheme 4.1 Waveguide arrays were generated in photopolymers comprising varying amounts of 2-hydroxethyl methacrylate (1), Silmer ACR A008-UP (2) and diethylene glycol diacrylate (3).

We first demonstrated that MI of an incandescent beam can be elicited in this newly developed photopolymer system. When launched into this photopolymerizable medium, a collimated, broad beam of incandescent light underwent modulation instability (MI) and spontaneously transformed into a large population (~10,000 cm⁻²) of self-trapped filaments. Figure 4.1 is a scheme of the optical assembly adapted from previous studies²⁴ for this experiment; light emitted from a quartz-tungsten-halogen (QTH) lamp was collimated by a plano-convex lens and launched onto the optically flat, transparent entrance face of a cell containing the photopolymerizable sample. The spatial intensity profile of the beam at the exit face of the cell was imaged through a plano-convex lens pair onto a high resolution CCD camera and monitored over time.



Figure 4.1 Optical assembly employed for MI-induced filamentation and waveguide generation. Light emitted by a quartz-tungsten halogen (QTH) lamp is collimated by a plano-convex lens (L1) and launched into the sample cell (S) containing the photopolymerizable fluid. The beam can be modulated by an amplitude mask (M) patterned with a square lattice ($\Lambda = 80 \ \mu$ m) of 40 μ m-wide apertures. The spatial intensity profile at the exit face of S is imaged onto a charge-coupled device camera (CCD) by a pair of plano-convex lenses (L2, L3). All lenses had a focal length = 25.0 cm. The inset contains two types of samples cells employed in experiments.

Spatial intensity profiles in Figure 4.2 trace the evolution of the uniform incandescent beam in the photopolymerizable fluid and show its striking transformation into a large population of discrete high-intensity spots. Each spot represents a tightly self-trapped filament of white light, which induces its own cylindrical waveguide and becomes entrapped as optical modes and in this way, propagates through the medium without diverging.



Figure 4.2 Modulation instability of an incandescent beam. 2-D and 3-D temporal evolution of the spatial intensity profile of an unmodulated, incandescent beam acquired at the exit face (path-length = 6.0 mm) of a sample cell containing photopolymerizable fluid. Color intensity scales are provided.

The mechanisms of MI have been extensively detailed elsewhere.^{18,19,23,24} Briefly, when launched into the photopolymerizable fluid, the white light beam initiates free-radical polymerization of methacrylate and diacrylate moieties. The resulting increase in density and thereby, the index of refraction (Δn) pushes the system into the nonlinear regime. Under these conditions, noise – normally negligible modulations in intensity – that is inherent to the optical field becomes greatly amplified. This originates from a

positive feedback cycle where light spontaneously concentrates within spatially localized regions that possess even a minor enhancement of Δn relative to their surroundings. The consequent increase in intensity leads to a greater extent of polymerization and Δn within these regions, which in turn become efficient at attracting additional optical intensity and further increasing Δn . As intensity modulations grow in this way, the optical field becomes unstable and spontaneously collapses into the ensemble of self-trapped filaments shown in Figure 4.2c; the filaments were statistically identical with an average diameter = 41 µm ± 6 µm.

These results confirm that free-radical polymerization in this newly developed system elicits MI of the incandescent beam. Because the process is seeded by noise, the filaments are randomly positioned in space (Figure 4.2c). For our objective of generating flexible waveguide arrays, we employed an amplitude mask consisting of a square lattice ($\Lambda = 80$ µm) of 40 µm-wide apertures to pattern the beam at the entrance face of the sample cell (Figure 4.3). Importantly, the 40 µm aperture width is commensurate with the inherent diameter of MI-induced filaments and ensures that the mask serves to impose a spatially controlled form of noise on the beam. Under linear conditions (prior to polymerization), the modulations imposed by the mask become "washed out" due to the natural divergence of the beam along the 5 mm path-length of the sample. Divergence is particularly significant for the incandescent beam, as it is incoherent in space and time. As a result, at t = 0 s, the beam appears only weakly patterned at the sample exit face (Figure 4.3a). As photopolymerization proceeds over the next 900 s, modulations imposed by the amplitude

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mask become amplified and the beam transforms into a highly ordered square lattice of self-trapped filaments.



Figure 4.3 Modulation instability of an incandescent beam. 2-D and 3-D temporal evolution of the spatial intensity profile of a spatially modulated incandescent beam acquired at the exit face (path-length = 6.0 mm) of a sample cell containing photopolymerizable fluid with composition Silmer:HEMA = 3:1 and 20 wt.% DEGDA cross-linker. Color intensity scales are provided. Scale bar in (a) = $200 \mu \text{m}$ applies to all images.

The square lattice of self-trapped filaments inscribed the corresponding array of multimode, channel waveguides into the photopolymerizable fluid, which transforms during this process into a free-standing, flexible and transparent monolith. Optical micrographs of the sample after polymerization provide proof of the square lattice of waveguides (Figure 4.4); the micrograph acquired in reflection mode of the exit face of the sample (Figure 4.4a) reveals the square array of waveguides with $\Lambda = -83 \mu m$, which is commensurate with the periodicity of its parent filament lattice (Figure 4i). In transmission mode, the waveguides capture and guide light from the microscope probe beam, which gives rise to the bright spots observed in the corresponding transmission micrograph (Figure 4.4b). Micrographs of the longitudinal cross-section of the sample reveal the cylindrical geometry of the waveguides, which propagate through the 5.0 mm path-length while a magnified image highlights the circular geometry of the waveguide output faces.

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Figure 4.4 Optical micrographs of a free-standing, waveguide array induced in a photopolymerizable fluid with composition Silmer:HEMA = 3:1 and 20 wt.% DEGDA cross-linker. Micrographs were acquired of the transverse cross-section in (a) reflection mode (b) transmission mode, of the (c) longitudinal cross-section in transmission mode and (d) of the transmission cross-section at greater magnification. Scale bar = $200 \,\mu\text{m}$ in all images.

4.4 <u>Waveguide arrays with varying flexibility</u>

Waveguide arrays were generated with hardness values ranging over an order of

magnitude (Shore-OO durometer of 9 ± 5 to 94 ± 2) by modifying the composition of the

photopolymer. This was achieved by either varying (a) the amount of the DEGDA crosslinker from 1 wt. % to 20 wt. % while retaining the Silmer:HEMA ratio at 3:1 or (b) varying the Silmer:HEMA ratio between 3:2 and 4:1 while keeping the DEGDA concentration at 1 wt. %. Tabulated Shore-OO hardness values for each composition and corresponding plots are provided in Table 4.1 and Figure 4.5, respectively. We generated MI-induced waveguide arrays in each of the compositions listed in Table 1. Spatial intensity profiles of an incandescent beam upon MI-induced filamentation in select compositions with wide-ranging values of hardness are provided in Figure 4.6. Systems containing a Silmer:HEMA ratio \leq 3:2 became slightly opaque upon photopolymerization, which in turn led to a decrease in the number of filaments that propagated without attenuation to the sample exit face (Figure 4.6d); MI-induced filamentation was efficient at all other compositions (Figure 4.6e-f) and appeared to be independent of the amount of DEGDA crosslinker in the medium (a-c).

Composition number	Silmer [% w.t.]	HEMA [% w.t.]	DEGDA [% w.t.]	Shore Hardness Reading
1	60.0	20.0	20.0	93.3 ± 2.0
2	67.5	22.5	10.0	77.5 ± 8.4
3	71.3	23.7	5.0	63.4 ± 5.5
4	74.3	24.7	1.0	31.5 ± 7.2
5	59.4	39.6	1.0	93.5 ± 2.0
6	66.0	33.0	1.0	69.1 ± 10.7
7	79.2	19.8	1.0	9.2 ± 5.0

Table 4.1 Compositions of photopolymers and durometer values of corresponding waveguide arrays.



Figure 4.5 Shore Hardness (Type-OO) readings for free-standing waveguide arrays generated from photopolymers with varying amounts of DEGDA crosslinker (blue) and varying ratios of Silmer:HEMA.



Figure 4.6 2-D and 3-D spatial intensity profiles of MI-induced self-trapped filaments in photopolymerizable fluids with (a-c) Silmer:HEMA ratio = 3:1 and DEGDA crosslinker amounts of (a) 10 wt.%, (b) 5 wt.% and (c) 1 wt.% and (d-f) with a DEGDA cross-linker amounts of 1 wt. % and Silmer:HEMA ratios of (d) 3:2, (e) 2:1 and (f) 4:1.

MI-induced filamentation resulted in free-standing waveguide arrays in each of the photopolymerizable fluids listed in Table 1. Shore-OO durometer measurements revealed that the arrays possessed significantly different values of hardness. As observed in Figure 6, the hardness of waveguide arrays increased from 32 ± 7 to 94 ± 2 as the amount of DEGDA crosslinker was increased from 1 wt.% to 20 wt. % while keeping the Silmer:HEMA ratio at 3:1; this increase in hardness is characteristic of highly crosslinked matrices, which are rigid and inflexible and limit the mobility and conformational changes of their constituent polymer chains and therefore, macroscopic flexibility.^{25–27} The relative amounts of Silmer and HEMA also had a significant impact on hardness; hardness values increased from 9 ± 5 to 94 ± 2.0 as the Silmer:HEMA ratio shifted from

4:1 to 3:2. This is consistent with hardness values of the individually polymerized Silmer and HEMA components, which were 29 and 81, respectively. We also note that the cylindrical geometry of the waveguides did not induce anisotropy in the hardness of the arrays; Shore-OO hardness values did not differ significantly between directions perpendicular or parallel to the waveguide propagation axes. For example, waveguide arrays with composition 2 had comparable hardness along all three axes (76 ± 8 , 76 ± 11 , 81 ± 5).

4.5 Light guiding properties of flexible waveguide arrays

Significant to our objective of generating flexible waveguide arrays, samples with Shore OO durometers ranging from only 9 ± 5 to 78 ± 8 were generated in photopolymers with low degrees of cross-linking (amount of DEGDA crosslinker ≤ 10 wt. %) (Table 4.1). Importantly, these hardness values are significantly smaller than those of the organosiloxane-based photopolymers, which have been extensively employed in studies of MI;²⁴ the latter are hard, rigid materials with durometers > 95.

To examine their light guiding properties, we selected waveguide arrays generated from photopolymer compositions with Silmer:HEMA ratio of 2:1 containing 4 wt. % to 10 wt. % DEGDA cross-linker. We reasoned that these compositions would balance small values of hardness that render them flexible with a sufficiently crosslinked matrix that would tolerate reversible compression. Importantly, these compositions also exhibit highly efficient MI-induced filamentation and corresponding waveguide formation. Photographs in Figure 4.7 qualitatively compare the far-field output of red laser beam propagating through photopolymer monolith containing 10 wt. % DEGDA cross-linker that was (a) unstructured and (b) contained a self-induced array of waveguides. The output of the former, as expected, retains an approximately circular spatial intensity profile as it propagates through the uniform beam. In the latter, the beam divides into multiple filaments as it becomes entrapped as optical modes within individual self-induced waveguides. These multiple filaments propagate without diverging through the medium and are observed in a far field as a square lattice of bright spots.



Figure 4.7 Photographs of the far-field profile of a hand-held red laser beam propagating through a 10 mm-long photopolymer monolith with composition Silmer:HEMA 2:1 with 10 wt.% DEGDA cross-linker (a) without waveguides and (b) containing an array of waveguides.

To demonstrate its flexibility, we subjected a waveguide array to multiple cycles of compression and decompression while monitoring its optical output *in situ*. For this experiment, we selected the array generated in a matrix with a relatively small degree of cross-linking (4 wt. % DEGDA crosslinker). As shown in the sequence of photographs in Figure 4.8, uniaxial pressure was exerted on the sample using a micrometer-controlled piston-head and the output of waveguides was imaged onto a high resolution CCD camera. Magnified images show that the waveguides continue to guide and transmit

incandescent light even as they are compressed to up to 86 % of their original separation distance (up to 70 % compression could be achieved (*vide infra*)). Once pressure was removed, the array immediately relaxed to its original position and this behavior was repeated over multiple cycles of compression and decompression. Figure 4.9 quantifies this process by plotting the average separation distance between waveguides in the array over three compression-decompression cycles. The average inter-waveguide distance prior to compression of 70 μ m decreased significantly to 50 μ m when the array was fully compressed. At the end of three cycles, the separation distance returned to 70 μ m, indicating complete recovery of the waveguide array after multiple cycles of compression.



Figure 4.8 Compression and decompression cycle of a free-standing array of waveguides generated in a photopolymer with composition Silmer:HEMA = 2:1 and DEGDA cross-linker = 4 wt. %. (a-c) photographs showing the waveguide (a) prior to (b) during and (c) after uniaxial compression of the waveguide array by manual application of a piston with (d-f) simultaneously acquired spatial intensity profiles of a uniform incandescent beam that was launched through the sample. Magnified regions are shown for clarity.



Figure 4.9 Changes in the average waveguide separation distance during three cycles of uniaxial compression and decompression of a waveguide arrays generated from a photopolymer with composition Silmer:HEMA 2:1 with 4 wt.% DEGDA cross-linker.

4.6 Conclusions

We developed a single-step, room temperature technique based on the modulation instability of an incandescent beam in a photopolymerizable fluid to generate freestanding arrays of cylindrical, multimode waveguides with square symmetry. Employing only incandescent light and an acrylate-based photopolymerizable fluid with a tunable composition, it was possible to generate waveguide arrays with hardness values ranging over an order of magnitude from Shore OO 9 ± 5 to 94 ± 2 . These included flexible arrays that could be reversibly compressed to up to 70 % of their original lattice periodicity; the arrays exhibited 100 % recovery after multiple cycles of compression and decompression.

4.7 Experimental Section

Materials: HEMA and DEGDA (Sigma Aldrich), Silmer (Siltech Inc.) and Irgacure 784[®] (donated by Ciba Specialty Chemicals Inc.) were used without further purification. Photopolymerizable fluids with compositions listed in Table 4.1 and each containing 0.05 wt. % Irgacure 784[®] were mixed for a minimum of 6 h by a DS-500 orbital shaker. The homogenized solution was slightly viscous, transparent and orange in color.

Optical experiments were carried out on the assembly shown in Figure 4.1. In a typical experiment, an incandescent beam ($\lambda = 320$ nm to 800 nm; ~1 mWcm⁻²) emitted by a quartz-tungsten-halogen (QTH) lamp (Cole-Parmer, USA) was collimated by a plano-convex lens (f. l. = 250 mm, d = 25.4 mm) and passed through a 2-D periodic amplitude mask ($\Lambda = 80 \mu$ m), which was placed flush with the entrance face of an optically transparent cell (pathlength (z) = 5.0 mm) containing the photopolymerizable epoxide sol. The spatial intensity profile at the exit face of the sample cell (z = 2.0 mm) was imaged through a pair of plano-convex lenses onto a high-resolution, progressive scan, charged-coupled device (CCD) (2040 pixels (H) x 1532 pixels (V) with a resolution of 3.2µm pixel⁻¹; sensitivity range = 350 nm to 1150 nm; WinCamDTM digital camera, Data Ray Inc., USA).

Structural characterization: A reflection microscope (Carl Zeiss, Canada; SteREO Discovery.V12)), and a transmission/reflection microscope (Olympus, USA; BX51 Upright, QImaging Retiga EXi Camera) were employed to acquire micrographs of free-

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standing waveguide arrays. Hardness readings were obtained through a Shore type-OO durometer (Rex Gauge Company Inc., USA). For these measurements, photopolymerized samples were extracted from a 10 mm-path-length transparent cuvette, cleaved with a scalpel into a 1000 mm³ cube. Hardness measurements were recorded along all three axes.

4.8 Acknowledgements

Funding from the Natural Sciences and Engineering Research Council, Canadian Foundation for Innovation and McMaster University is gratefully acknowledged. We thank CIBA GEIGY, Canada, for the generous donation of photoinitiator, IRGACURE-784[®].

4.9 Appendix: Diamine crosslinked polymer system

A copolymer system was investigated that exhibited similar mechanical properties to the surfactant-based polymer system. It is based on an acrylate-functionalized silicone with an amine-terminated poly(propylene glycol) crosslinker. Two variations of the system were investigated: using a homopolymer silicone with each monomer containing an acrylate group, or using a copolymer silicone with a portion of monomers containing an acrylate group and mixed with an acrylate-terminated silicone (Scheme 4.2). Both systems were sensitized to light using Irgacure 784.



Scheme 4.2 Chemical composition of the two amine-crosslinked silicone systems.

The solutions were mixed and added into 10 mm x 10 mm cuvettes to be left in the dark to cure for 24 hours. Both compositions solidified upon curing but retained the yellow colouration. Optical experiments were conducted as described previously in this chapter without an amplitude mask and using a power of 1.0 mW. However, evidence of MI was not observable in the intensity profile; this is because the opacity of the sample rapidly increased (Fig. 4.10a). Interestingly, this increased opacity is anisotropic; when looking at the sample perpendicular to the propagation axis, it is transparent near the exit face (Fig. 4.10b). Furthermore, evidence that MI did in fact occur is seen when looking at

micrographs of this region, where the embedded structure can be seen through to the exit face (Fig. 4.10c).



Figure 4.10 Experimental results of irradiation of silicone systems. (a) Beam intensity profile at the exit face of the silicone sample at four different time intervals, showing the rapid decreasing in intensity. (b) Photographs of the resulting sample looking along (left) and perpendicular (right) of the propagation axis. (c) Optical micrograph of the silicone sample near the exit face. [In (a), 1 pixel = 9.3 μ m; in (c), scale bar = 200 μ m]

This anisotropic opacity is caused by rapid polymerization at the entrance face of the sample. As this process is a frontal polymerization¹⁹, monomers near the entrance face will be irradiated and begin reacting first. If this occurs too rapidly, the material will become denser in this region compared to the rest of the sample. This generates highly crosslinked polymers that are big enough to scatter light and reduce the transparency. As more and more monomers are consumed, this effect becomes lessened further into the sample in addition to the reduction of light intensity getting through to it. The overall

result is the observed opacity at the entrance face while still allowing MI to occur further into the sample (as the desired balance between diffraction and refraction is achieved). Evidence of this proposed mechanism is seen by the decreased rate of opacity forming when a lower intensity of light is used. This was not studied more extensively as these lower intensities did not result in as distinct of structures. Changes to the chemical composition, such as reducing the number of acrylate groups present, could provide an avenue to reducing the anisotropic opacity while still allowing MI to occur.

4.10 <u>References</u>

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5 Hydrogel-based optical and cell scaffold structured material

5.1 Abstract

Hydrogels have been extensively studied as the basis for artificial cell scaffolds but there are a limited number of methods capable of adding structures that may guide cell growth. Furthermore, use of them in optical systems has focused mostly on generating fibers or slab waveguides from the material. Nonlinear optical phenomena, such as modulation instability and self-trapping, open facile pathways to easily generate large populations of embedded light channels in photopolymerizable hydrogels. Microstructures were formed in the material through optimization of the chemical and optical parameters and the effect swelling had on these structures was characterized. Preliminary water transport and cell seeding experiments were performed on the surface of the samples to assess their viability as a cell scaffold. Unidirectional swelling of the hydrogel resulted in the formation of a plano-convex lens with a dynamically tunable focal length and enhanced angle of view due to the embedded waveguides.

5.2 Introduction

The inherent nature and versatility of hydrogels has lead to their implementation in a wide variety of fields, including biomedical^{1–3}, drug delivery⁴, and food additives⁵. These crosslinked polymer networks can be swollen with water without dissolving and provide structural stability to the resulting material^{6–8}. Because a significant portion of the hydrogel is made up of water, they can closely mimic natural tissue while offering greater control of the chemistry. For these reasons, extensive research has looked to produce synthetic cell scaffolds from hydrogels^{9–13}. The pores created in the polymer network

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upon swelling are able to encapsulate cells and give the material high biocompatibility and oxygen permeability, which is critical for tissue growth¹⁴.

Along a similar vein, hydrogels have been used to create optical components that can be interfaced with biological systems^{15–18}. Because hydrogels can be formed into specific designs (ie. thin films, long fibres, etc.), they can be easily adapted to the desired optical system while retaining their inherent biocompability. A specific example of this is the formation of dynamically tunable microlenses, where changes in swelling of the hydrogel will alter the focal length of the individual lenses^{19,20}. These differ from more traditional dynamic lenses, other than size, in that the change in focal length functions as an "on/off" rather than tuning to a specific one in order to focus on an object^{21,22}. However, the construction of hydrogel lens is preferable since they are a single component rather than a liquid-filled chamber with a flexible membrane.

To prepare the hydrogels for these various applications, photopolymerization of the crosslinks is commonly conducted. This method offers good control on the shape and strength of the resulting material at low costs. This also means that the hydrogel can act as a nonlinear material as the crosslinks will increase the refractive index as they are formed. Nonlinear optical phenomena, such as modulation instability and self-trapping, require this slow refractive index change to occur and because the polymerization reaction is irreversible, will create permanent structures within the material^{23–25}.

The work presented in this chapter demonstrates the ability to induce MI and selftrapping in a photopolymerizable hydrogel and explores the possibility of utilizing the resulting material as a structured cell scaffold and enhanced, dynamic optical lens.

5.3 Experimental

5.3.1 Functionalization of poly(ethylene glycol) diacrylate polymer

Poly(ethylene glycol) (PEG) from Sigma-Aldrich ($M_n = 4,600$ Da), triethylamine (TEA) from VWR (M. W. = 101.19 g mol⁻¹), and acryloyl chloride from Sigma-Aldrich (M. W. = 90.51 g mol⁻¹) were added to dry dichloromethane under nitrogen gas in a 1:2:4 molar ratio. The reaction was left overnight then rinsed with 1.5 M potassium carbonate and phase separated overnight. The PEGDA-containing organic layer was collected and subsequently dried with sodium sulphate. After filtering out the sodium sulphate and concentrating the solution via rotary evaporation, the solution was precipitated in cold diethyl ether. The PEGDA product was collected by filtration, allowed to dry overnight and then dried under vacuum. The product was a white powder and characterized by NMR (Figure 5.1).



Scheme 5.1 Functionalization of poly(ethylene) glycol with acryloyl chloride.



Figure 5.1 1H NMR of poly(ethylene) glycol diacrylate in CDCl₃. The percent acrylation was determined by comparing the integral for the allyl protons (5.83 to 6.40 ppm) to the integral for the polymer backbone protons (4.30 ppm).

5.3.2 Preparation of PEG-based hydrogel solution

Poly(ethylene glycol) diacrylate (PEGDA) from Sigma-Aldrich ($M_n = 700 \text{ Da}$), triethanolamine (TEOA) from Sigma-Aldrich (M. W. = 149.19 g mol⁻¹), Eosin Y (EY) from Sigma-Aldrich (M. W. = 647.89 g mol⁻¹) and n-vinyl pyrrolidone (NVP) from Sigma-Aldrich (M.W. = 111.14 g mol⁻¹) were used as received. PEGDA (either 700 Da or 4,600 Da) was mixed with deionized water or 1.5 M disodium phosphate/monosodium phosphate buffer (pH = 8) at varying concentrations, ranging from 10% w/v to 50% w/v. Either 225 mM or 0.1% v/v of TEOA, as well as either 0.05 or 0.01 mM of EY, were stirred into the solution. Additionally, some solutions contained various concentrations (18.5-111 mM) of NVP. The resulting solutions were transparent, pink in colour, and had a low viscosity.



Scheme 5.2 Chemical components of the hydrogel system.

5.3.3 Optical experiments

Samples were polymerized on an optical assembly as described here: A quartztungsten-halogen lamp (Cole-Parmer 9741-20, Illinois, USA) was used as a light source. A plano-convex lens (FL = 25 cm) collimated the light onto a sample cell (path length = 5 to 10 mm) containing the PEG-based hydrogel solution. The light beam intensity exiting the sample was focused onto a high-resolution charge-coupled device (CCD) camera (WinCamDTM, DataRay Inc., USA) using two plano-convex lenses with different configurations: both of equal focal length (FL= 25 cm) to give 1.0X magnification, and each with a different focal length (lens 1 FL = 10 cm, lens 2 FL = 25 cm) to give 2.5X magnification. All components were mounted on an optical rail with carriers for 0.25 mm resolution positioning.



Figure 5.2 Schematic of the optical assembly. A broad beam of incoherent white light is produced by the QTH lamp and collimated by a plano-convex lens (L1). An amplitude mask (M) can be placed in front of the sample (S) to modulate the light. Two plano-convex lenses (L2, L3) image the beam profile onto a CCD camera. INSET shows the two types of sample cells used, with corresponding measurements.

5.3.4 Swelling experiments

After irradiation, the glass cover slips were removed from the sample cell, with gelled samples used for swelling studies taken out of the cell. The samples were submerged in water for a minimum of 2 hours. After all studies involving the swelling properties of the material were completed, samples were maintained through submergence in water and sealing of the container. The degree of swelling for hydrogel samples was determined by weighing fully deswelled samples, allowing them to swell at room temperature for 4 hours, then weighing the swelled samples. The ratio of the two weights was then calculated. Water uptake of the material was monitored by swelling samples with a

solution containing $1.0 \ge 10^{-4}$ M fluorescein isothiocyanate (FITC). Samples were both uniformly and unidirectionally swelled and analyzed via fluorescence microscopy.

5.3.5 Preparation of 3T3 fibroblast cell cultures

NIH3T3 fibroblast cell lines (Cell Biolabs, I) were pre-warmed at 37 °C and cultured in a solution containing high glucose DMEM, 10% FBS, 0.1 mM of NEAA and 2 mM of L-glutamine. The culturing was conducted according to the procedure provided by Cell Biolab, Inc. The cells were placed on a tissue culture dish and kept in a 37 °C incubator for seven days. The cell cultures were characterized using a cell counter and microscopy. The cultured cells were trypsinized, centrifuged for 5 minutes and re-suspended in the fresh medium for later use.

5.3.6 Integration of cell cultures into hydrogel scaffold

Hydrogel samples were sterilized via ethanol soaking and irradiation with UV light. Some of the samples were soaked in a solution containing fibronectin (50-100 mg/mL) overnight to increase cell adhesion. All samples were then placed in the medium containing the 3T3 fibroblast cells for 2 days at 37 °C. After removal from the medium, the hydrogel samples were rinsed with PBS to remove any unattached cells.

5.3.7 Acceptance angle range and angle of view measurements

Hydrogel samples were analyzed in a custom optical assembly (Figure 5.3) as described here: a tungsten-halogen lamp (Ocean Optics, LS-1) was used as the light source. A beam was launched onto the front side of the sample. The sample was held in an adjustable lens holder. To image the light exiting the sample, two configurations were used depending on the geometry of the sample. For plano-convex samples, a CCD camera

was positioned at the focal point of the sample as calculated based on its dimensions. For planar samples, two plano-convex lenses (FL = 25 cm) imaged the beam at the exit face of the sample onto a CCD camera. All components were fixed on an optical rail with carriers for 0.25 mm resolution positioning, and fixed on an optical table at a point directly beneath the sample. The rail was rotated about this point, with the position where the camera is in line with the beam considered 0°. The acceptance angle range was determined by measuring the peak width at $1/e^2$, while angle of view was determined by measuring the peak width at zero intensity.



Figure 5.3 Schematic of optical set-up used to measure fields of view for (A) flat and (B) curved samples.

5.3.8 Characterization

A transmission/reflection microscope from Olympus, USA (BX51 Upright,

QImaging Retiga EXi camera) was used to characterize the structures within the polymer

samples as well as the uptake of FITC using a fluorescence filter ($\lambda_{ex} = 490$ nm, $\lambda_{em} =$

525). Beam intensity profiles were collected using DataRay software (DataRay Inc.,

USA) and were processed using either SigmaPlot 10.0 (Systat Software Inc., USA) or

Python 3.6 (Python Software Foundation). Filament diameters were measured at the full width at half maximum (FWHM) using ImageJ (National Institutes of Health).

5.4 <u>Results and Discussion</u>

5.4.1 Development of self-trapping & MI in a PEG-based hydrogel

Initial experiments were conducted to determine the parameters required for the formation of waveguides within the hydrogel material. The ideal parameters for the concentration (and molecular weight in the case of PEGDA) of the four components in the hydrogel solution and the irradiation procedure were determined based on the emergence of filamentation in the intensity profile as well as characterisation of the waveguides via micrographs. Utilizing both characterisation techniques became crucial for optimization of the material due to the appearance of anisotropic opacity in the materials, as previously discussed in 4.9. Briefly, as light enters the system, rapid polymerization occurs at the entrance face of the sample. This generates highly dense regions of crosslinked polymer in a localized area that will scatter light and cause this front region to become opaque. The effect each component of hydrogel formation has on the emergence of both waveguides and the opacity is outlined below. It has been previously established that the molecular weight of PEG used to form the hydrogel will directly impact the opacity of the resulting material. Therefore, initial studies were conducted to determine the optimal molecular weight of PEG for waveguide formation. The two different molecular weights of PEGDA used, 700 Da and 4,600 Da, were able to produce gelled samples containing large populations of waveguides, as confirmed by microscopy. However, characterisation of the intensity profiles and visual inspection of

each shows a significant increase in opacity at the entrance face for samples prepared with 700 Da PEGDA compared to those prepared with 4,600 Da PEGDA.

Analogous to this, the concentration of NVP had a substantial effect on the emergence of opacity in the samples. NVP was used exclusively for samples made with 4,600 Da as samples without it did not gel. Four concentrations (18.5 mM, 37 mM, 72 mM and 111 mM) were used to produce hydrogel samples containing waveguides; the frontal opacity however greatly decreased with concentration. This is in line with the prediction that rapid densification at the entrance face is the cause of decreased light transmission as it has ben previously established that NVP concentration has a strong correlation with the polymerization rate of acrylate monomers. The effect of these two components on the resulting intensity profile is shown in Figure 5.4, with further analysis of the NVP concentration shown in Figure 5.5. The effect of the two components in the photoinitiator system was determined through sequential decreases to their concentration. No decrease to the opacity was seen at lower concentration, suggesting Eosin Y and TEOA do not significantly contribute to the densification of the material and strictly initiate the reaction. Finally, the weight percent of PEGDA was varied from 8% to 30% and did not contribute to the opacity problem, although it had a significant impact on the physical properties of the material (an effect that will be discussed further in 5.3.4).



Figure 5.4 Temporal evolution of beam profile propagating through hydrogel samples. The samples contain (A) 700 Da PEGDA at 15% w. t., (B) 4,600 Da PEGDA at 10% w. t. with 18.5 mM NVP, and (C) 4,600 Da PEGDA at 10% w. t. with 111 mM NVP. [Scale bars = 1,000 um]



Figure 5.5 The effect of NVP concentration on the opacity of the material. The concentrations of NVP used were 111 mM (blue), 72 mM (red), 37 mM (green), and 18.5 (purple). With higher NVP concentration, the integrated intensity of the beam profile decreases at a greater rate. Experiments were conducted until any patterns were lost in the profile.

The final component of the hydrogel formation was the irradiation and its corresponding parameters. This includes the power of light used, the irradiation time, as well as the inclusion of a pre-polymerization step. For initial experiments involving the 4,600 Da PEG, the power of the beam was set to approximately 5.5 mW for MI experiments and 2.5 mW for multifilament self-trapping experiments (where a horizontal amplitude mask was used to break up the broad beam). However, even at 18.5 mM NVP, the frontal opacity would still occur in the sample. The power was lowered down to 0.6 mW but still showed no improvement, with the opacity still occurring within 10 minutes of irradiation. Based on hypothesized cause of the problem, it was proposed that uniformly irradiating the sample and causing gelation prior to the generation of MI/self-trapping could slow the reaction throughout the material and minimize the opacity.

Initially, samples were irradiated at different time lengths, ranging from 2 to 6 minutes, to see when gelation had begun. This was determined by placing a small magnetic stirrer in the sample cell, allowing it to stir during irradiation and observing when stirring was no longer occurring. The time required for gelation depended on the specifics of the hydrogel solution being used, such as PEGDA weight percentage or NVP concentration. The gelled samples were then placed in the optical assembly and irradiated as previous samples had been. However, these samples showed very little evidence of self-trapping or MI as it appeared this process limited the available monomers too significantly.

During this process, other parameters for the experiments were manipulated and it was found that a stronger response could be obtained from the material when a 2dimensional amplitude mask (horizontal and vertical patterning) was used. With a beam power of 1.1 mW, significant filamentation would occur without the occurrence of frontal opacity in the material. Despite this, the response was not as distinct as with previous photopolymerizable materials, although significant structuring could be seen within the material. This suggested that the nonlinear response to light only occurred after a certain degree of polymerization has occurred in the material. Based on this observation, a short pre-gelling irradiation step (30-60 s at 10 mW) was introduced to start the polymerization throughout the sample without causing significant gelling. With the introduction of this step, a beam power between 1.6 to 3.0 mW (depending on the specific degree of functionalization for PEGDA) was found to give the strongest filamentation for self-trapping and MI. These experiments showed no increased opacity at the front of the sample and filamentation was typically observed within 20 minutes of irradiation.



Figure 5.6 Evidence of self-trapping (A, B) and MI (C, D) in the hydrogel system with 15% w.t. of PEGDA. Intensity profiles (A, C) show the light's response to the material, and the optical micrographs (B, D) show the resulting structures. The waveguide structure is formed throughout a 10 mm sample, as shown in the composite micrograph in E. [Scale bars in A-D = 200 μ m, in E = 500 μ m]

5.4.2 Improvements to the experimental procedure

Experiments were conducted to alleviate lifetime issues that would reduce the effectiveness of hydrogel solutions that were approximately a week old. These solutions exhibited significantly lower waveguide formation and slower polymerization time. The initial hypothesis was that the humidity or pH of the solution was changing over time and were affecting the components of the solution. The pH of solutions with varying age was

determined it was seen that older ones were significantly more acidic. Freshly prepared solutions are basic ($pH \sim 8$) due to the presence of triethanolamine in the solution, whereas week-old solution is acidic ($pH \sim 6$). It was predicted that this change in pH was affecting the interaction between eosin Y and triethanolamine in the photoinitiator system.

It was hypothesized that the formation of carbonic acid from aqueous CO_2 in solution was causing the decrease in pH. In order to test this and increase the lifetime of the solutions, nitrogen gas was bubbled through the freshly prepared solution and the vial filled with nitrogen gas. Solutions were left for one week and self-trapping experiments were conducted, with all other parameters remaining the same. The solution showed significantly more waveguide formation and polymerization time compared to week-old solution not kept under nitrogen gas, and it was also comparable to freshly prepared solution. A phosphate buffer was used in place of the water in the hydrogel solution to maintain the pH more consistently than the nitrogen bubbling. The buffer showed no impedance to waveguide formation and allowed samples to be produced at least two weeks after the hydrogel solution was prepared.

The characterization of the resulting filaments produced in the hydrogel was also improved through adjustments in the imaging set-up. More specifically, it was observed that the filaments produced during self-trapping and MI were smaller in diameter than in previous systems and when an amplitude mask is used, splitting of the filaments can occur (as evident in Figure 5.6A and B). This made it difficult to characterize their size with 1:1 imaging as the resolution of the CCD camera (9.3 µm per pixel) was close to

their observed FWHM ($\sim 20 \,\mu$ m). The magnification of the set-up was increased to 2.5x through changes to the imaging lenses and to obtain a more resolved profile of the light. A previously used photopolymer system, MAPTMS, and the hydrogel system underwent MI while using the 2.5x imaging and the average filament diameter was measured. Additionally, self-trapping using the 2-dimensional amplitude mask was conducted on the hydrogel. The self-trapping experiment confirmed that the filaments were splitting in the hydrogel system and the MI experiments showed the two systems have significantly different average diameters ($29 \pm 7 \mu m$ for the hydrogel, $38 \pm 10 \mu m$ for the MAPTMS system). Furthermore, the filaments are much more densely packed in the hydrogel (160 filaments/mm² vs 76 filaments/mm²), which may explain why the filaments would want to split within those regions. Because there is a direct correlation between the nonlinear change in the material and the perturbation dimensions from MI, it would suggest that the refractive index difference for the hydrogel and for MAPTMS is significantly different. Further investigations into this phenomenon could provide a more precise explanation and further insight into the relationship between filament size and the photopolymerization.



Figure 5.7 Characterization of filament size and distribution in hydrogel material. Intensity profiles show the difference in filaments generated by MI for (A) MAPTMS and (B) the PEGDA hydrogel. The splitting of filaments during self-trapping is more clearly seen when comparing (C) 1.0X magnification to (D) 2.5X magnification. [All scale bars = $200 \ \mu\text{m}$]

5.4.3 <u>Preparation and testing of hydrogel samples for use as cell scaffold</u>

5.4.3.1 Swelling dynamics of hydrogel samples

The various parameters related to the swelling of the hydrogel were investigated to

better understand the chemical nature of structures produced in the hydrogel. It was

hypothesized that cells would be able to differentiate between the polymer density in the

waveguides and surrounding area, and thus subsequently position themselves

preferentially. If there is a big enough difference in the polymer density, it could also cause differential swelling and water uptake. The parameters chosen to investigate this were the weight percent of PEGDA, the size and distribution of the waveguides, and the uptake of a water-soluble fluorescent dye.

As previously mentioned, the weight percent of PEGDA used to form the hydrogel samples was varied to optimize the formation of waveguides. Although the compositions were comparable in their ability to elicit MI and self-trapping, the degree of swelling changed significantly with the amount of PEGDA used. The degree of swelling for hydrogels made with 10% w.t. PEGDA was 12.36 ± 1.58 whereas the value for samples made with 15% w.t. PEGDA was 7.59 ± 2.59 . The degree of swelling was not measured for samples containing 30% w.t. PEGDA as they were not viable for cell studies, however the samples were much stiffer and appeared to swell less than those with lower amounts of PEGDA.

With this information, the effect that swelling has on the embedded structure was investigated. 10% w.t. PEGDA was predominantly used for these experiments due to its greater degree of swelling and biocompatibility. Samples containing structures produced via self-trapping were monitored using microscopy and beam profiling while they were swelled and deswelled (Figure 5.8). It was seen that the embedded structure would change in response to the materials state of swelling, with the spacing and dimensions of the structure decreasing during deswelling and recovering back to its initial parameters upon reswelling. Deswelling of the material caused the periodicity of the structure to decrease from $78 \pm 1.2 \mu m$ to $73 \pm 3.0 \mu m$ after 1.5 hours, then to $36 \pm 2.1 \mu m$ after 17

hours. Upon reswelling, the material is restored to its initial parameters, with the periodicity of the structure recovering to $71 \pm 2.7 \ \mu m$ (91%) after 44 hours. This shows a clear connection between the polymer networks formed in the hydrogel and the microstructures generated within the sample, which may be utilized for preferential cell positioning. Furthermore, it demonstrates the material's ability to dynamically change the way it interacts with light based on how swollen it is. This phenomenon could be utilized further with a more responsive hydrogel or one that responds to an external stimulus.



Figure 5.8 The change in the microstructure dimensions over time as the hydrogel deswells (A, C) and reswells (B, D). These changes are seen in both the beam profile (A, B) and optical micrographs (C, D). [Scale bars = $200 \ \mu$ m]

Having shown that there exists a connection between the chemical network and the embedded structure, it was proposed that the formation of the structure would cause the generation of regions with different local chemistry. More specifically, the waveguides in the material would have a slightly higher degree of polymerization than the interstitial regions and thus would be more hydrophobic, due to the inherent nature of PEG. To investigate this, a solution containing a water-soluble fluorescent dye, FITC, was used to swell hydrogel samples and compare the fluorescent response in different regions. Because this response is proportional to the concentration of dye, the more fluorescent regions will have had more of the initial solution transported there via capillary forces. Samples that were uniformly swelled showed distinction in their fluorescent response that was comparable in positioning to the pattern seen under reflection microscopy. This would suggest that preferential uptake had occurred but it was difficult to distinguish between reflections from the structure and response from the dye (Figure 5.9A and B). To help with this issue, samples were then swelled unidirectionally where only one face of the sample was exposed to the dyed solution. This approach was adapted from Fan et al. for measuring diffusivity in hydrogel samples. In this instance, the distribution of the dye throughout the material was characterized rather than the depth of diffusion. Unfortunately, it was difficult to resolve any differences in the fluorescence response in the micrographs (Figure 5.9C and D). This may be due to the thickness of the samples or the density of waveguides, or the difference in chemical nature between the waveguides and surrounding area is not sufficient to elicit preferential water uptake. Further tests with this material or different hydrogel systems may provide more insight on this relationship.





5.4.3.2 Interfacing of biological species with hydrogel

Microstructured hydrogel samples were prepared via self-trapping with sample depths of 2 and 3 mm. These were the smallest depths where structuring could be formed and were chosen for cell studies as to minimize the material the cells would have to potentially travel through. Preliminary studies involved seeding the cells on one of the surfaces of the samples and examining their position relative in the embedded structure and their movement into the material. The cells were able to proliferate and survive on the surface of the samples showing the self-trapping process did not compromise the biocompatibility of the material. However, it was not possible to determine the cells' positioning as they did not adhere to the material and thus washed away during the workup of the samples. In an attempt to facilitate adhesion, samples were swelled with a solution containing fibronectin, a cell binding protein. Unfortunately, the interactions between the polymer network and fibronectin were not strong enough and the protein also washed away upon workup.

5.4.4 Hydrogel dynamic lens formation and characterization

During the design and optimization process of the unidirectional swelling, an interesting observation was made. Samples that were contained within glass cells would form a domed shape on the side that was swelled (Figure 5.10). This occurs because of the adhesion between the glass walls and the hydrogel material; the high water content of the material means there is significant hydrogen bonding between the two surfaces. As the material swells on the exposed side, this adhesion restrains the edges while the centre is free to expand and results in the observed curved face. This observation is the basis for a hydrogel-based optical lens with an embedded structure and a dynamic focal length.



Figure 5.10 Photograph of hydrogel sample demonstrating the curved architecture upon unidirectional swelling.

Initial experiments explored the effect this behaviour had on the embedded structure. Curved samples were generated containing waveguides that ran parallel to the swollen face and characterized via beam profiling and optical micrographs. Similar to the behaviour demonstrated in 5.3.3.1, the embedded features responded to the swelling and curved in the direction of the swelling (Figure 5.11). The angle of the bend in the waveguides was higher in regions closer to the curved face compared to further away, suggesting this process causes the material to swell non-uniformly. This is further confirmed when looking along the propagation axis of the waveguides after the material is swelled. Waveguides in the bottom half of the sample (where minimal swelling has occurred) appear in the expected square pattern, whereas ones in the top half have been expanded along the swelling axis and appear merged with neighbouring waveguides above and below them. This unique structuring to an array of waveguides has not been seen before in photopolymers, especially when considering that it can be reverted into a linear structure by deswelling the material.



Figure 5.11 Demonstration of curved waveguide structure in a unidirectionally swelled hydrogel sample. Composites of micrographs (A) and intensity profiles (B) of the whole of the sample, with individual micrographs of the top (C) and bottom (D) of the sample, show the change in curvature in the sample. The expansion of the ends of the waveguides can be seen by comparing the intensity profiles at the exit face of the sample (E) before and (F) after swelling. [Scale bars in A, B = 1000 μ m; in C, D = 500 μ m; in E, F = 200 μ m]

To fully characterize and implement a hydrogel-based dynamic lens, two changes to the previous experiment were made. The first was to change to a cylindrical sample cell, as this would result in a final geometry of the lens that would be more comparable to standard glass lenses and thus the lensmaker equation could be used to compare the two. The second change was to inscribe the waveguides perpendicular to the swollen face of the sample rather than parallel as this would cause the incident light to be affected by both the geometry of the material as well as the light-guiding capabilities of the structure. Samples were polymerized using the same method as previous samples but with a vertically orientated optical assembly to achieve these changes. Both structured and unstructured samples were successfully gelled and then swelled into the desired curved shape. Solutions containing 15% w.t. PEGDA were predominately used for the lens samples as they provided the best balance between swellability and rigidity of the material. Analysis of the dynamic lens samples looked at three characteristics that would demonstrate the feasibility of and improvements provided by these lenses. The characteristics include the generation of a focal point, a change in curvature upon swelling/deswelling, and the effect the waveguides have on the lens' field of view. In addition to generating a focal point, the corresponding focal length should match the calculated value from the lensmaker equation based on its physical dimensions. Satisfying the first characteristic, a distinct focal point is seen when broad, uniform incoherent beam is launched through the plano-convex sample and occurs at the expected focal length (Figure 5.12A). For one specific sample, the dimensions of the sample gave a calculated back focal length (BFL) of 15.0 mm with the corresponding measured BFL being 14.0 mm, showing strong agreement. Additionally, the waveguide structure was retained within the material, with the imposed square pattern seen all along the curved face of the sample (Figure 5.12B).

Upon confirmation of this, the change in curvature was then analyzed by taking plano-convex samples and cycling them between swollen and deswollen states. All samples were able to undergo this process, although some samples only showed a change in thickness and not in curvature. This occurred due to hydrogel material separating from the back glass wall of the sample cell and filling with water, preventing the middle of the sample from retracting. Samples that did not show this, however, showed a distinct ability to change curvature over multiple cycles (Figure 5.12C-F) without significant degradation to the material. This allows for dynamic control of the lens' focal length through changes to the material's state of swelling. The maximum radius of curvature for samples was

achieved after 2-3 days, while a return to a planar configuration was obtained after 1 day; changes to the chemical composition (predominately the weight percent of PEGDA) of the hydrogel would affect these rates. Hydrogels with 15% w.t. PEGDA had a maximum radius of curvature of 8.39 ± 1.06 and would be reduced to 0 after deswelling.



Figure 5.12 Hydrogel samples exhibiting dynamic lens characteristics. Intensity profiles show how the samples affect a beam of light (A) at the focal length of the sample and (B) at the entrance face. Photographs of the hydrogel sample show the change in curvature at four different time points: (C) after polymerization, (D) after 3 days in water, (E) after 1 day in air, and (F) after 3 days back in water. [Scale bars in A, B = 200 μ m; in C-F = 2000 μ m]

Having shown the material's ability to act as a dynamic lens, the impact the

embedded waveguide structure has on the lens' inherent properties was investigated.

Specifically, the effect it has on the angle of view of the lens was studied. Because of the

nature of the waveguides, it is expected that incident light at angles greater than the

calculated angle of view would be coupled into the waveguides near the edge of the

sample. Within their acceptance angle, light would be coupled into the waveguides and

carried into the lens since they conform to the shape. The overall structure and optics of the lens would then refract the light into the focal point. This would overall result in light staying on the detector beyond the expected angle of view. To see this effect, three different lenses were compared: a standard glass lens with a focal length comparable to the hydrogel samples, a polymerized hydrogel sample with no embedded structure, and a polymerized hydrogel sample with an array of waveguides. The angle of view was experimentally determined for each and compared to their corresponding calculated values. Additionally, hydrogel samples in the planar configuration, either with an embedded structure or without, were analyzed to determine the inherent acceptance angle range of the hydrogel waveguides. Two different configurations of the optical assembly were used for plano-convex and planar samples for two reasons: the use of imaging lenses would influence the angle of view measurements as they themselves have an angle of view, however they are needed to accurately image the beam at the exit face of the sample for the acceptance angle measurements.

The acceptance angle range of the waveguides in the hydrogel was measured to quantify the light collection capability of the structure and give an approximation to the effect it would have on the lens' angle of view. The acceptance angle range of the waveguides was found to be $2.6 \pm 0.1^{\circ}$, an increase of 0.5° on the unstructured material (Figure 5.13A). This is relatively low compared to other polymeric materials used for these measurements²⁶ but is expected as this system has significantly fewer polymerizable groups and thus would generate a smaller change in refractive index. This means the waveguides are closer in refractive index compared to the surrounding area and

thus have a less of a propensity to cause total internal reflection. Despite this, the structure still exhibits increased light collection and thus could affect the angle of view of a lens.

With this information, the angle of view was measured for the different lens samples. The first angle of view measurement was taken for the glass lens; as it is very precisely designed and fabricated, the measured and expected value should be the same. This acted as confirmation that the modified optical assembly was accurately measuring the angle of view. The lens, with a focal length of 25.4 mm, had a calculated value of 14.6° and a measured value of 15.0°. This small disparity is expected as accurate measurements were only obtainable at every 0.5°. With confirmation of the validity of the technique, measurements of the angle of view for the structured and unstructured hydrogel lenses generated from a 15% w.t. PEGDA solution were collected and analyzed. For the unstructured sample, a lens with a focal length of 22.4 mm was used and had a calculated angle of view of 16.6°. The measured value was found to be 16.5°, showing good agreement with the calculated and further confirms the hydrogel lens samples are able to follow standard lens measures. The structured lens, having a focal length of 21.6 mm and calculated angle of view of 17.2°, showed distinct enhancement to the light collection and gave a measured value of 20.0° . This 1.8° increase is comparable to the acceptance angle of the waveguides and similar increases were seen for three other structured lens samples with different focal lengths. The embedded waveguides appear to be producing the desired effect of directing additional light into the lens to then be focused.



Figure 5.13 Characterization of the structured hydrogel lens' light guiding capabilities. Normalized integrated intensity values at various angles are plotted and show (A) the acceptance angle range for a single waveguide in a structured sample (in black) and the corresponding region in an unstructured sample (in red). The angle of view is plotted for (B) a glass lens, (C) a hydrogel lens without structure, and (D) a hydrogel lens with structure, with each of their corresponding expected angle denoted by red dotted lines.

5.5 <u>Summary</u>

In this work, a hydrogel material was produced containing a large population of lightguiding channels using modulation instability and self-trapping of light. This result alone is substantial as it shows a material with a very low percentage of polymerizable groups is capable of eliciting these responses in light and opens up possibilities to generate structures in this fashion in a wider variety of polymeric materials than previously assumed. Manipulation of the hydrogel's composition and experimental parameters lead to optimization of the process and a greater understanding of the factors involved in forming these structures. The initial goal of the project was to produce a synthetic cell scaffold that would provide directionality to the cells' growth. Initial studies were conducted for preferential swelling and seeding of 3T3 mouse fibroblasts on the surface of the hydrogel but the results were inconclusive. Instead, the development of a structured dynamic lens was investigated after discovering that the hydrogel samples took on a plano-convex configuration upon unidirectional swelling. With a multi-waveguide structure embedded in the lens, enhancement to the angle of view was observed compared to the unstructured lens without impeding the lens' ability to dynamically change its focal length based on the degree of swelling. This style of lens may open avenues to more sophisticated optical systems that are more compact, have fewer mechanical parts and are able to extend beyond the boundaries of traditional optics.

5.6 <u>References</u>

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6 **Conclusions**

The unique interactions that occur between light and nonlinear materials have generated substantial research interest for many years. These materials are able to cause light to behave in ways that cannot be achieved with linear media. Some of these behaviours include the self-trapping of light or modulation instability of a beam; both of these involve the suppression of a beam of light's natural tendency to diverge. Consequentially, the local properties of the material will change in specific ways to affect the light's propagation. These changes are irreversible in certain nonlinear media, such as photopolymers, and thus permanent structures are left embedded within material. The primary goal of this thesis is to investigate how beam interactions and different polymer systems can affect these structures, as well as exploring new ways of utilizing the resulting samples.

6.1 <u>Self-organized lattices in photopolymer systems</u>

Initial studies looked at the filament interactions that occur between orthogonal beams undergoing MI in a photopolymer [Chapter 2]. Mutually incoherent broad white light beams were launched simultaneously into a photopolymerizsable medium and their resulting beam profiles were analyzed to characterize how the beams influenced each other. Filaments generated by a single beam undergoing MI are spatially positioned at random, with their position originating from noise in the material or fluctuations in the beam. When a second beam is then introduced, and the two beams propagate simultaneously, the filaments from each beam will interact with their orthogonal counterparts and align into rows along their propagation axis. The waveguides inscribed

by the filaments into the polymer (due to the irreversible nature of the polymerization reaction) intersect and form stacks of square grids throughout the material. By introducing a third orthogonal beam, filament alignment is achieved in both the vertical and horizontal axis of each beam and their arrangement takes on a square symmetry. The resulting waveguides will again intersect and generate a cubic lattice throughout the material. This is a fairly counterintuitive result as mutual incoherence between the beams is giving rise to a highly ordered structure. It is hypothesized that intensity overlap of nearby orthogonal filaments will drive them into alignment due to increased refractive index in these regions. This forms the basis of the mechanism for this process and is confirmed by tracking the filaments' position over time. This process is not isolated to orthogonal filaments and alignment can also be elicited with beams set at non-90° angles.

6.2 <u>A photoresponsive material that computes with light</u>

By now controlling where the filament populations can interact within the material, unique patterns can be generated in the resulting intensity profiles. These controlled interactions can be used to perform data recognition and transfer, all-optical encoding, and basic arithmetic [Chapter 3]. The basis of these operations is the four distinct types of filament alignment that can be achieved in the intensity profile, which includes randomly positioned filaments, 1-dimensionally aligned filaments along the horizontal or vertical axis, and 2-dimensionally aligned filaments. By patterning orthogonal beams with a binary sequence of dark and bright stripes (*encoders*) and launching them with an unpatterned beam (*carriers*), filament interactions become localized and the polymer sample can be divided into voxels that contain one of the four types of alignment. The

first process, data recognition and transfer, is achieved by launching two beams simultaneously and imposing an alternating pattern of bright and dark stripes onto one of the beams. The resulting pattern of the carrier filaments matches that of the imposed one, alternating between disordered and 1-dimensionally ordered filaments. This demonstrates the material's ability to recognize the information inputted in one beam and transfer it to a second one. When a second encoder population is introduced, active operations can be conducted where the material takes the two inputs and produces a result based on them. The first instance of this is volumetric encoding, where the information imprinted into the encoder population directly determines the configuration of the carrier filaments in each voxel. The encoded information can be retrieved by analyzing each voxels' read-out and translating back to whether there was horizontal or vertical input. This method offers a 2^{N} -fold increase in capacity compared to conventional encoding and can be easily quantified in a single step via FFT analysis. The final and most significant capability of this system is to perform two fundamental operations of binary arithmetic. By reading the antidiagonal voxels in the output, the sum of the binary strings inputted into the two populations of encoder filaments can be determined. Each voxel is assigned a value (0, 1, 1)0C1) based on the filament ordering contained within it and the string constructed from these values is the sum. Subtraction is performed in a similar manner but applies the two's complement method to determine the difference. The working principles of this method can be expanded to other nonlinear systems or light sources, such as LEDs, because of the universality of the dynamics involved.

6.3 Soft, flexible waveguide lattices in a photopolymer

Having established these novel methods for the manipulation of incoherent light beams, investigations into different polymeric systems capable of eliciting MI and selftrapping were conducted. There were two main motivations for this: improve the physical properties of the resulting material compared to the systems currently used, and add new functionality to the embedded waveguide structure. The first polymer system looking to achieve this was one based on an organosiloxane-based surfactant [Chapter 4]. In addition to the surfactant (Silmer), a crosslinking agent (DEGDA) and copolymer (HEMA) were used to offer further control of the chemical composition. This system utilizes a longer chain poly(ethylene oxide) spacer between the siloxane and acrylate groups compared to previous systems to reduce the rigidity and hardness of the resulting polymer samples. Both MI and self-trapping of incoherent light were seen in the polymer, and permanent structures were left embedded in the resulting material. The samples were far more robust compared to those made from MAPTMS and did not suffer from aging or degradation. The versatility of the system was demonstrated by changing the percentage of each polymeric component and showing that self-trapping could still be elicited. The changes did however alter the bulk physical properties of the resulting samples, as expected, with increased crosslinker or a larger ratio of HEMA over ACR causing the material to become harder. This offered better control of the rigidity of the material than previously possible and allowed for the generation of flexible waveguide arrays. The light guiding capabilities of these arrays were tested by coupling light into them and applying a compression force. They were able to continue guiding light after significant deformation
and return to their initial dimensions upon removal of the force. The structure is robust enough to persist after many cycles of compression with no permanent defects in the shape, size or arrangement of the waveguides. These results demonstrate the material is capable of housing a large array of durable, flexible waveguides which can be easily manipulated and continue to control light's propagation.

6.4 Dynamic lens and cell scaffold based on waveguide-embedded hydrogel

The second system studied was chosen with the intention of developing a cell scaffold that could elicit guided cell growth [Chapter 5]. A poly(ethylene glycol)-based hydrogel material was chosen for this as it has the desirable biocompatibility and physical properties to serve as a cell scaffold while still capable of being formed via photopolymerization. Specifically, poly(ethylene glycol) diacrylate was used as the basis with a water-soluble, low cytotoxicity photoinitiator system chosen to initiate the polymerization reaction. In order for the waveguide structure to be formed throughout the material, it required optimization of both the chemical composition of the hydrogel solution as well as the irradiation parameters. The result was a soft, highly flexible material with an embedded structure running throughout it and the capability to change size via swelling or deswelling. The material was characterized in terms of the effect of swelling on the structure and the water uptake before introducing biological species to the surface and examining the interaction between the two. The structure showed a direct response to the swelling, with the spatial dimensions increasing or decreasing depending on the volume of water held within the hydrogel. However, it was difficult to observe preferential uptake of water into the sample and clearly demonstrate a distinct chemical

difference between the waveguides and the interstitial regions. Preliminary cell seeding tests were conducted with the structured hydrogel samples but were inconclusive, as the cells could not properly bind to the material. It was discovered, however, that unidirectional swelling of the hydrogel material would cause it to take on a plano-convex configuration and would behave as an optical lens. The benefit of this lens compared to more traditional ones is the ability to dynamically change the focal length and have light guiding channels embedded within. The focal point of hydrogel lens samples could be moved without degradation based on the swollen state of the material; the rate of this process depended on the composition of the hydrogel. The angle of view was measured for structured and unstructured hydrogel lenses to determine if there was enhancement due to the waveguides. There was a 1.8° increase in angle of view compared to the theoretical value when waveguides were present, whereas the unstructured lens showed no increase. These enhanced, dynamic lens may lead to more advanced optical systems in the future because of their properties.

6.5 General conclusions

This thesis provides significant contributions to the fields of nonlinear optics and polymeric materials. The first contribution is the understanding and development of a system that allows incoherent light sources to communicate with one another. This is a counterintuitive finding as no interference or signal mixing exists between the beams and thus could not interact in traditional linear media. However, the nature of the nonlinear medium allows changes to occur that each beam will see and adapt to. This discovery spurred on an encoding and computing system based on these interactions and may lead

to new advancements in optical communication. The second contribution is the demonstration of MI and self-trapping of incoherent light in a variety of photopolymerizable systems. This shows the universality of the process and allows for microstructures to be generated in materials with unique properties and characteristics. As long as a sufficient number of polymerizable groups exist, a large enough refractive index change can be elicited. The bulk polymer properties can then be dictated by additions or modifications to the rest of the monomer's chemical structure.

6.6 <u>Future work</u>

The work presented in this thesis establishes the working principles of the encoding and computing system based on incoherent MI filament interactions. The material used, however, suffers from lifetime deficiencies that limit the practicality of the method. A polymer system capable of producing more robust sample, such as the one used in Chapter 4, could be used in place. Additionally, the irreversibility of the chemical reaction, although beneficial for generating structures, means that multiple samples are needed to hold a large bank of different patterns. Investigations into a reversible polymerization reaction that can be sensitized to visible light would help alleviate this issue and could simplify the overall process.

6.6.1 Further investigations into MI in photopolymers

Further understanding of these filament interactions could be possible through modifications to the multiple beam experiments. More specifically, restrictions to the filament population may show further evidence of the migration that occurs during propagation through the material. It would become easier to see which filaments are

interacting and what is the degree of overlap required to initiate the migration. Knowing these values would become important for systems that have different sized filaments, such as the hydrogel [Chapter 5].

As shown in Chapter 3, light with a narrower range of wavelengths (such as that produced by LEDs) is capable of producing the expected patterns for the encoding and computing system. This was done using blue LEDs and showed more distinct filament alignment compared to the patterns obtained with white light. This could make analysis via FFT easier, as the corresponding periodicity peaks would be more intense, and so further experimentation should be conducted. The precise effect that wavelength has on the process could be determine and used to optimize the characterisation and read-out of the patterns.

6.6.2 Further optimization of waveguide-embedded flexible polymers

In terms of the polymer systems used to generate MI and self-trapping, tuning of the physical properties can be continued with the goal of producing a thin, flexible coating with embedded light guiding structures. Evidence of self-trapping occurring over short distances has been previously shown^{1,2} and so with changes to the chemical composition, a robust material that can be applied to number of shapes and surfaces could be produced. More extensive characterisation of the polymer's physical properties, such as the Young's modulus or glass transition temperature, would provide greater insight into its chemical nature and may suggest further changes to improve the structural stability.

6.6.3 Improvements and alterations to the hydrogel system

The waveguide embedded hydrogels offer the greatest number of opportunities for future research, both as a cell scaffold and a dynamic lens. In terms of its biological applications, the hydrogel was initially designed for this purpose so it is close in final chemical composition to what is required in terms of cytotoxicity and biocompatibility. However, cell-adhesive moieties need to be integrated into the chemical structure in order for cells to interact with the structure and hopefully migrate into the material. This can be achieved by attaching the RGD peptide sequence into the polymer backbone; this is the sequence within fibronectin responsible for cell attachment. By chemically bonding the peptide to the hydrogel, it is significantly more likely it will stay in the network and should greatly increase attachment of cells to the surface. Beyond this, more direct experimentation would be needed where the muscle cells are in solution before gelling of the sample. The impact of the structure on the cells' positioning would be clearer to see in this case as one would expect them to be driven into alignment as the waveguides are formed. Both this effect and survivability of the cells when fully encased in the hydrogel could be determined and would give a more definitive answer to the viability of this technique to generate guided cell growth. If successful, other cell types could be introduced in place of the muscle cells to verify the versatility of the hydrogel system.

The dynamic hydrogel lens represents an excellent proof of concept that has the potential to generate a new class of enhanced optics. The hydrogel used in these experiments, however, was optimized for biological applications and therefore suffered from structural instability. Replacing the material with a hydrogel capable of the same

degree of swelling but with more favourable physical properties would give the lens more stability and reproducibility. Furthermore, the process of swelling and deswelling the samples was quite time intensive, taking days to fully swell in some cases, and limits the dynamism of the lens. A possible way to address this is to use a hydrogel whose swelling/deswelling can be trigger by an external stimulus. More specifically, pH- and temperature-sensitive hydrogels have shown the ability to fully swell in a significantly shorter time, ranging from 2 hours down to 30 minutes, depending on the conditions the samples are introduced to $^{3-5}$. Using a material capable of this, while retaining the required transparency and ability to generate waveguides, would offer greater control of the curvature and consequently, the focal length of the lens. The final improvement would be utilizing a material that exhibits are greater change in refractive index upon gelling. This would result in waveguides with a higher refractive index, therefore would have a greater acceptance angle, and should theoretically increase the lens' angle of view. If a hydrogel system is designed that is able to incorporate all three of these improvements, the resulting lens would be a significant forward in the field of dynamic optics.

6.7 <u>References</u>

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