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Spontaneous Pattern Formation Due to Modulation Instability of Incoherent White Light in a Photopolymerizable Medium

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Abstract: Spontaneous pattern formation due to modulation instability was observed in a broad uniform beam of incoherent white light propagating in an optically isotropic, photopolymerizable organosiloxane. Pattern formation originates from intensity-dependent refractive index changes due to polymerization, which cause competition between the natural diffraction (broadening) and self-induced refraction of the beam. Under these nonlinear conditions, weak intensity modulations in the beam, noise, that would be negligible under linear conditions are amplified. The amplified patterns become unstable over time and spontaneously divide into individual self-trapped filaments of white light of essentially identical diameter (76 $\pm$ 3 μm), which propagate through the medium without diffracting. In the case of noise with a weak 1-D periodic modulation, for example, the uniform beam transformed into a 1-D periodic array of self-trapped lamellae, which in turn formed a 2-D array of self-trapped cylindrical filaments. Although the rate of pattern formation varied inversely with optical power (measured from 8.4 to 59.8 mW), the uniform beam always split into discrete filaments, demonstrating that they are the most stable form of light propagation under the nonlinear conditions created by polymerization. Each filament of light retained the spectral composition and incoherence of white light, which showed that the entire polychromatic, incoherent and unpolarized wavepacket collectively participated in pattern formation. These findings are consistent with recent theoretical models of nonlinear white light propagation and with experimental observations of pattern formation in coherent and partially coherent light. Because refractive index changes due to polymerization are permanent, pattern formation imparts microstructure to the organosiloxane. Optical micrographs revealed that, after pattern formation, the initially homogeneous medium consisted entirely of a closely packed array of narrow channel waveguides induced by self-trapped filaments.

Introduction

Recent studies showed that a narrow beam of incoherent white light self-trapped and propagated without diffracting (broadening) or weakening (in intensity) in a photopolymerizable organosiloxane medium.[1,2] Photoinitiated free-radical polymerization of methacrylate substituents caused refractive index changes, which opposed the natural diffraction of the beam. The beam therefore retained its original spatial intensity profile even as it propagated over long distances. The findings implied[2] that the same competition between diffraction and self-induced refraction would elicit spontaneous pattern formation due to weak modulation instabilities, noise,[3] in a broad, uniform beam of white light. The work reported here demonstrates that such a beam propagating in the initially homogeneous, optically isotropic organosiloxane transforms into a one-dimensional array of bright stripes, which in turn spontaneously form a stable two-dimensional array of bright spots. Each spot in this array corresponds to the cross-section of an individual self-trapped cylindrical filament of white light.

In a medium that exhibits photoinduced refractive index changes, a narrow beam of light will propagate in a self-induced channel waveguide. Under the same conditions, a broad uniform beam will spontaneously divide into a pattern composed of multiple self-trapped filaments. Each filament is similar to an individual self-trapped beam. This has been predicted by theoretical models and experimentally observed for coherent[4−11] and partially spatially coherent[11−18] light. The most recent and

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complex development in this field is the self-trapping and (separately) spontaneous pattern formation of white light, which is unpolarized, polychromatic, and, because it originates from an incandescent source, spatially and temporally incoherent.[19] A white light beam therefore consists of a distribution of intensity speckles that randomly fluctuates at the femtosecond timescale.[20] The collective propagation of the rapidly fluctuating wave packet either as a single narrow self-trapped beam or as spontaneously formed patterns across a broad beam has stimulated experimental[1,2,20,21] and extensive theoretical research.[22−29]

Periodic optical patterns are most commonly generated through the interference of multiple, mutually coherent beams. Spontaneous formation of patterns in a single broad beam of incoherent white light is therefore a particularly intriguing and counterintuitive problem. There are in fact extremely few experimental studies of pattern formation in white light. This is because a white light beam from an incandescent source would disintegrate in the conventional nonlinear materials that are predominantly employed in experiments of nonlinear light propagation. Because they originate from higher order dielectric susceptibility tensors, these media exhibit ultrafast photoresponses,[30,31] which are sensitive to rapid phase fluctuations and therefore inhibit the collective propagation of white light. Media with noninstantaneous responses by contrast would respond to a time-averaged (smoothed) intensity profile. Segev and coworkers demonstrated that such noninstantaneous photoresponses could be induced in photorefractive crystals at extremely low (nW) optical powers. This enabled self-trapping of a narrow focused beam of white light[20] and, subsequently, spontaneous pattern formation in a broad uniform beam of white light.[21]

The most recent studies of self-trapped white light have taken an entirely different approach.[1,2] Moving away from conventional nonlinear media, they employed instead a photoinitiated free-radical polymerization process, which responds to light intensity that is averaged over milliseconds to seconds during which random femtosecond-scale phase fluctuations are effectively cancelled out.[11,32] Because it originates from an inherently slow chemical reaction, the photoresponse in this system is always noninstantaneous, regardless of optical intensity. This enabled studies of the intensity dependence of the process through which it was possible to understand the evolution and dynamics of self-trapped white light beams.[2] Motivated by these findings, the studies presented here examine the spontaneous formation of patterns in a broad beam of white light and the corresponding permanent changes in refractive index and microstructure of the organosiloxane system.

Results and Discussion

Experimental Evidence of Spontaneous Pattern Formation. Pattern formation was studied with a broad beam of white light (400−800 nm) emitted by an incandescent quartz−tungsten−halogen (QTH) lamp. The randomly polarized, polychromatic, spatially and temporally incoherent light was collimated with a planoconvex lens into a broad beam with a uniform (top-hat) intensity profile (Figure S1, Supporting Information). The beam was shone uniformly onto the entire entrance face (10 mm × 10 mm) of organosiloxane sol contained in a transparent (320−800 nm) polymethylmethacrylate cuvette. The spatial intensity profile of the beam after it had propagated 6.00 mm in the medium was imaged onto a high-resolution, charge coupled device camera and monitored over time. The organosiloxane is optically isotropic and transparent to visible light.[33] In the absence of polymerization (that is, in organosiloxane without photoinitiator), the beam profile remained uniform for as long as it was observed (∼2300 s) (Figure S1, Supporting Information). Under these linear conditions, weak perturbations in the optical field, noise, become negligible with increasing propagation distance. This is because minor intensity variations weaken and disappear due to the natural diffraction of light. At 6.00 mm, the beam therefore appears unchanged from its form at the entrance face (0.00 mm).

The beam initiated free-radical polymerization of methacrylate substituents as it propagated in organosiloxane doped with free-radical titanocene photoinitiator (λ_{max} = 393, 460 nm). Consequent changes to its intensity profile at a propagation distance of 6.00 mm are presented in Figure 1. The corresponding movie (MOVIE_S1) and temporal evolution of 1-D cross-sections (Figure S2) are presented as Supporting Information. Within 385 s, the uniform beam (Figure 1a) developed bright (high intensity) and dark (low intensity) stripes (Figure 1b). The contrast (modulation depth) of the 1-D pattern increased over time (396−418 s) due to the increase and decrease of intensity in the bright and dark stripes, respectively (Figure 1c−e). During the same time period, the bright stripes developed minor, random variations in intensity, which in turn became amplified and ultimately caused each stripe to spontaneously divide into spots. The modulation depth of the spots increased with time; at 550 s (Figure 1g), the initially uniform beam had transformed into a 2-D array of discrete, bright spots. A magnified 3-D profile (Figure 1g, inset) shows that each spot has an intensity maximum (peak). Although the absolute intensity of spots changed over time, their spatial position and size remained unchanged for the duration of the experiment (Figure 1d−g).

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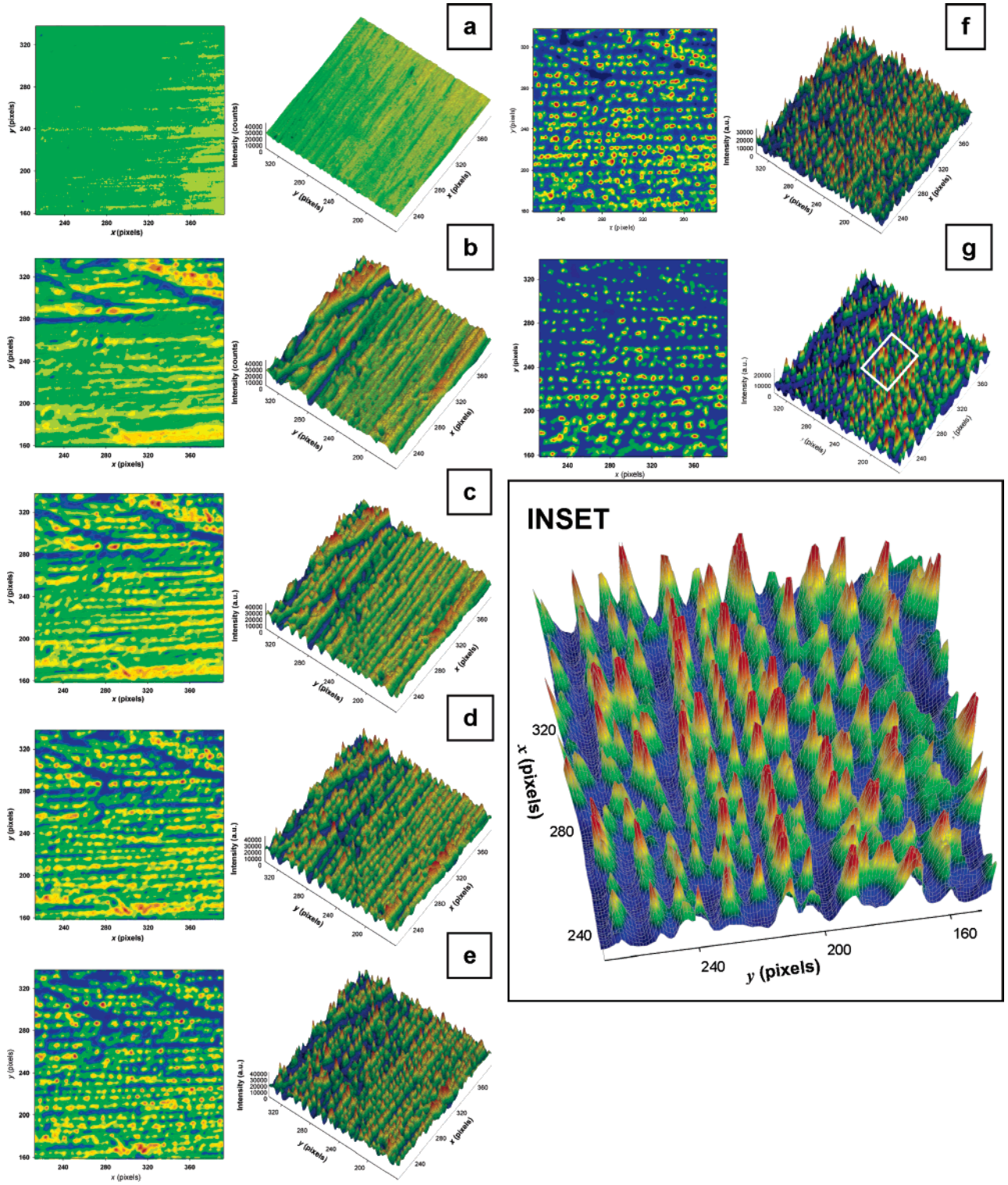

Figure 1. Temporal evolution of the 2-D and 3-D spatial intensity profiles of (a) a uniform beam of white light at a propagation distance of 6.00 mm in photopolymerizable organosiloxane contained in a polymethylmethacrylate cuvette at (b) 385 s, (c) 396 s, (d) 407 s, (e) 418 s, (f) 473 s, and (g) 550 s. The inset is a magnified intensity profile of individual self-trapped filaments of white light at 550 s. Striations of the cuvette were oriented along the *x*-axis. For clarity, intensities were normalized to the maximum peak in images f and g (1 pixel = 9.3 μm × 9.3 μm). (The complete sequence of images is available as MovieS1, Supporting Information.)

Mechanism of Pattern Formation: Competition between Diffraction and Self-Induced Refraction. The white light beam initiates methacrylate polymerization and corresponding positive changes in refractive index, which are strongly localized in space.[33,34] Because the polymerization rate is directly proportional to intensity,[32] index changes maximize in the most intense regions of the optical field. Light is confined more efficiently in areas of higher index,[35] leading in turn to greater local

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intensity. The rate of index change consequently increases further in these regions, causing even tighter entrapment of light. Polymerization in this way effects a reciprocal and nonlinear interaction between optical intensity and refractive index change. In this nonlinear regime, competition develops between the natural diffraction and self-induced refraction of the beam, refraction being strongest in regions of greatest intensity. As a result, any spatial variation in intensity is actually preserved during propagation. For example, it was previously shown that, under these conditions, a narrow white light beam with an intensity gradient self-trapped and propagated without diffracting in a self-induced gradient-index channel waveguide.[1,2]

The same principle underlies spontaneous pattern formation in a broad beam. Because of polymerization, even minor intensity variations (noise) across the beam, that under linear conditions would be negligible, become self-trapped. Noise originates from weak variations in refractive index encountered by the beam. For example, striations at the crystal-face seeded pattern formation of partially coherent light in a photorefractive crystal.[12] In the experiments presented here, the birefringent, faintly striated wall of the polymethylmethacrylate cuvette containing the organosiloxane imposed a 1-D intensity modulation on the white light beam (Figure S3, Supporting Information).[36] The intensity modulation is negligible under linear conditions and cannot be detected at a propagation distance of 6.00 mm (Figure S1, Supporting Information). In the presence of polymerization, however, the modulation induces a weak 1-D (layered) variation in refractive index at the entrance face (0.00 mm). Because light preferentially occupies regions of (even infinitesimally) greater index, intensity that had initially been distributed uniformly partitions into layers with slightly greater index. Because of the nonlinear photoresponse of the medium, the rate of change of refractive index within these layers is greater than the surrounding regions. As a result, light is most efficiently confined within the high-index layers and propagates as self-trapped lamellae. This process is observed as the transformation of the uniform beam into a periodic pattern of bright (high-index) and dark (low-index) stripes at propagation distance 6.00 mm (Figure 1b); the bright stripes correspond to the intensity cross-sections of the self-trapped lamellae. As the refractive index continues to increase nonlinearly, light leaks from low-index regions and accumulates within the high-index layers, causing the increase in modulation depth of the pattern observed in Figure 1b−e.

While the 1-D periodic pattern of stripes in the beam is seeded by the microstructured cuvette wall, the splitting of each bright stripe into bright spots is the truly spontaneous event in the pattern formation process. In other words, there is no predetermined modulation of intensity that seeds pattern formation in this second dimension. In fact, the intensity variations that render each bright stripe unstable and initiate its transformation into spots are random (Figure 1d−g). They probably originate from local concentration fluctuations and convection in the medium caused by the evolving exothermic polymerization reaction. However, the spots once formed have a narrow size distribution, with an average diameter (measured over an area of 2500 μm × 2500 μm over 24 experiments) of 76 ± 3 μm (Table 2). A magnified 3-D intensity profile highlights the striking contrast between the uniform beam and its ultimate intensity distribution in a 2-D array of spots (inset, Figure 1g). Each spot corresponds to the transverse cross-section of an individual self-trapped filament of light, which propagates through its own self-induced channel waveguide in the medium.

(36) This was confirmed by tilting the cuvette with respect to the optical axis, which caused a corresponding tilt in the orientation of bright stripes.

Table 1. Spot Size Corresponding to Self-Trapped Filaments Measured over an Area ~2500 μm × 2500 μm[a]

source of noise	spot diameter (μm)	number of experiments
striations of PMMA cuvette	76 ± 3	24
isotropic glass cuvette	76 ± 5	28
amplitude mask (1-D, 80 μm modulation along *y*)	65 ± 6	3
amplitude mask (1-D, 80 μm modulation along *x*)	66 ± 5	4

[a] The value was averaged over a given number of experiments carried out under different types of noise or intensity modulations imposed on the broad beam of white light.

Table 2. Time Taken for the Formation of Bright Stripes (t_1) and Bright Spots (t_2) at Different Powers of the White Light Beam[a]

optical power (mW)	t_1 (s)	t_2 (s)	spot size (μm)
8.4	473 ± 50	781 ± 110	75 ± 8
12.8	440 ± 40	929 ± 403	71 ± 8
15.9	712 ± 260	865 ± 367	72 ± 10
23.0	493 ± 130	551 ± 153	70 ± 8
28.1	262 ± 68	284 ± 75	92 ± 10
36.4	201 ± 13	225 ± 9	85 ± 8
50.5	150 ± 16	187 ± 8	77 ± 8
59.8	146 ± 29	169 ± 43	68 ± 9

[a] The average spot size of self-trapped filaments acquired at each power is also included. Results at each power are averaged over at least three experiments. (The standard deviation of t_1 and t_2 values at relatively lower powers (≤23.0 mW) is large due to the much more gradual transition of stripes to spots at these powers; by contrast, the transition is more abrupt at higher powers, leading to smaller errors.)

Multiple Self-Trapped Filaments of Incoherent White Light. A fundamental characteristic of pattern formation is that a perturbation in the intensity of a broad beam seeds its transformation into multiple self-trapped filaments. The transformation is spontaneous because each self-trapped filament is similar to a self-trapped beam, which as predicted theoretically[22−29] and observed experimentally[1,2,20] is the most stable form of a narrow beam in the same nonlinear conditions. In the first (and only other) experimental example of pattern formation in incoherent white light, a uniform beam transformed into filaments as it propagated in a photorefractive crystal.[21] Pattern formation of white light in the organosiloxane follows the same pathway and leads to stable self-trapped filaments. Remarkably, the array of filaments emerges in an optical field, which is itself polychromatic and incoherent in space and time. This transformation is moreover a collective process: the entire wavepacket simultaneously participated in pattern formation. As a result, light contained within each filament was itself incoherent. No apertures were introduced in the path of the white light beam emitted by the QTH lamp; its coherence length (calculated according to $\theta \approx \lambda/\pi l_c$[21] to be 0.31 μm at λ = 600 nm) is significantly smaller than the average width of the self-trapped filament (76 ± 3 μm). To further confirm that each filament was composed of white light, pattern formation was monitored sequentially through three filters that spanned the visible spectrum. Figure 2a−c shows intensity profiles after spot formation acquired in the spectral ranges between 400−515 nm (blue), 515−550 nm (green), and 610−800 nm (red); for comparison, the corresponding image acquired without a filter

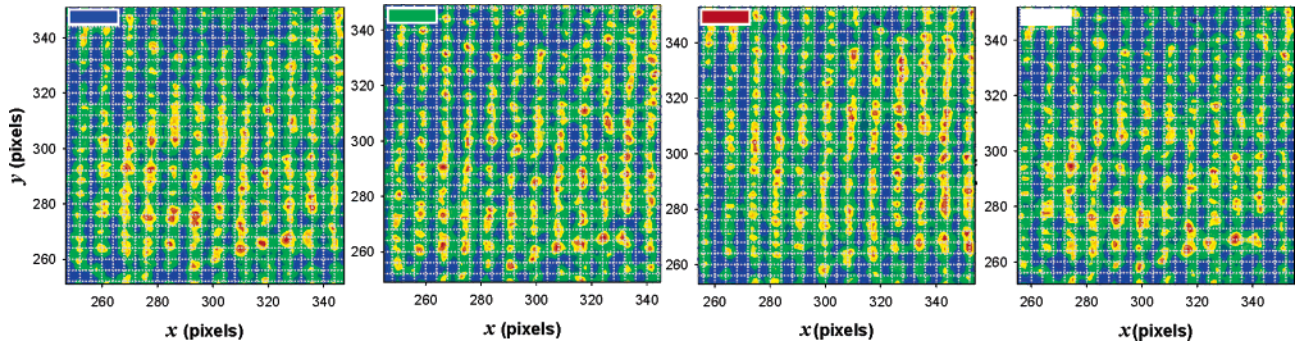

Figure 2. Two-dimensional spatial intensity profiles of self-trapped filaments (bright spots) observed through blue (400−515 nm), green (515−550 nm), and red (610−800 nm) filters. The profile acquired over the entire visible spectrum (400−800 nm) is included for comparison (1 pixel = 9.3 μm × 9.3 μm).

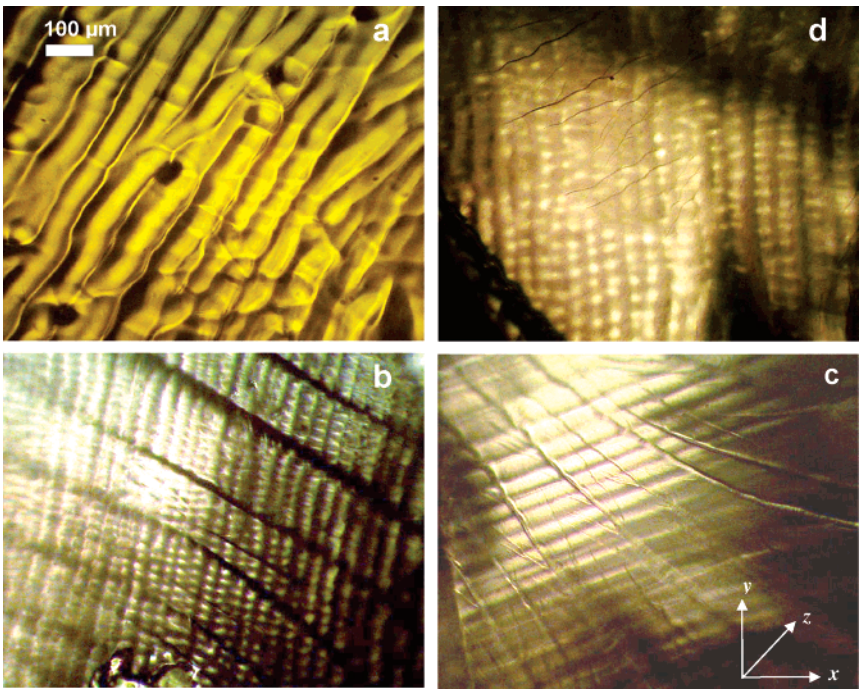

Figure 3. Optical micrographs of the organosiloxane gel after transformation of the uniform white light beam into bright stripes, with (a) transverse ($x-y$) cross-section and bright spots, and (b) transverse ($x-y$) and (c) longitudinal ($y-z$) cross-sections. Micrograph (d) shows that the microscope probe beam is selectively guided through the channel waveguide cores. All transverse cross-sections were acquired at a distance of 6.00 mm from the entrance face. (The diagonal lines in (b) and (c) are fractures/wrinkles introduced during sample preparation.)

(averaged over 400−800 nm) is included (Figure 2d). The spatial distribution of relative intensity in all three spectral regions was the same; that is, there was no significant separation of wavelengths. These two observations are consistent with the theoretical model recently developed by Buljan and co-workers.[29] The model predicts that all frequencies constituting white light become unstable simultaneously and, consequently, the spectral composition of the optical field is the same at all stages of pattern formation.

The above findings also correlate to previous observations of the self-trapping of a narrow beam of white light in the same system; the spectral composition and incoherence of white light was also retained at all stages of this process.[1,2] This was possible because the photoresponse of the organosiloxane satisfies the three prerequisites for self-trapping of white light.[22] In addition to a (1) noninstantaneous response that effectively cancels out phase fluctuations, the photoresponse permits (2) growth of a multimoded waveguide that supports all of the multiple optical modes constituting white light (to conserve optical power) and satisfies the condition of (3) self-consistency, in which the time-averaged distribution of guided modes remains correlated to the time-averaged distribution of the white light modes. Because each self-trapped filament is similar to a single self-trapped beam of white light, the same three prerequisites must also be satisfied for spontaneous pattern formation in white light.

Permanent Photoinduced Changes in Refractive Index and Microstructure of the Organosiloxane. Because they originate from an irreversible polymerization reaction, refractive index changes induced by white light are permanently imprinted in the organosiloxane medium. (By contrast, photoinduced index changes due to the Kerr or Pockel's effect originate from higher order dielectric susceptibility tensors and decay once the optical field is removed.) Upon exposure to white light, the fluid organosiloxane transformed into a gel, which was wholly extracted from the cuvette at different stages of pattern formation and observed under a transmission optical microscope. Micrographs in Figure 3 show transverse (a, c, d) and longitudinal (b) cross-sections of the gel. The former were acquired at the plane corresponding to the propagation distance of 6.00 mm.

Images were acquired after the first transition of the beam into bright stripes (a) and its second transition to bright spots (b−d).

The pattern formation process imparts microstructure to the organosiloxane, which prior to irradiation is homogeneous and optically isotropic. The layered microstructure in Figure 3a was induced by the 1-D intensity modulation of the beam; each layer corresponds to the transverse cross-section of a planar waveguide that traps and guides a fraction, self-trapped lamella, of the white light beam. Accordingly, the width of each layer (∼85 μm)[37] corresponds to the average width (measured over 12 experiments to be 95 ± 5 μm) of each bright stripe (Figure 3). The micrograph in Figure 3 shows that, after the beam transforms into bright spots, circular high-index features develop along each layer, leading to a 2-D array of spots. The width of each spot (∼50 μm)[37] is comparable to the average width of bright spots (measured over 24 experiments to be 76 ± 3 μm) observed in Figure 1. A micrograph of the longitudinal cross-section (Figure 3c) shows that the spots correspond to transverse cross-sections of cylindrical channels that propagate through the medium. These are the self-induced channel waveguides that trap and guide fractions of white light as individual self-trapped filaments. The micrograph in Figure 3d shows that, when aligned with the optical axis of the transmission microscope, each channel waveguide appears brightly lit. Because its refractive index is greater than its surroundings, each channel traps and (passively) guides over at least 6.00 mm a fraction of the white light of the probe beam from the microscope itself.

Power-Dependence of Spontaneous Pattern Formation. Spontaneous pattern formation of white light in the organosiloxane was observed at eight different optical powers ranging from 8.4 to 59.8 mW (Table 1). In all cases, the uniform beam transformed first into bright stripes and then to stable bright spots with essentially the same diameter (76 ± 3 μm). However, the time at which the uniform beam transformed to stripes (t_1) and then to spots (t_2) varied inversely with power; for example, the values (averaged over three experiments) of t_1 and t_2 at 8.4 mW were 473 ± 50 s and 781 ± 110 s, respectively. The corresponding values at 59.8 mW were only 146 ± 29 s and 169 ± 43 s (the conversion of stripes to spots at this power was almost instantaneous). Phenomenological models show an inverse relationship between optical intensity and the time taken to induce a specific change in refractive index in photopolymerizable systems.[38a,b] This is a consequence of free-radical polymerization kinetics, which dictates that the extent of polymerization is proportional to both optical power and time.[2,32] The inverse relationship between optical power and t_1 and t_2 indicates that critical changes in refractive index (Δn_1, Δn_2) must be achieved for each transition of the beam to take place. At greater optical powers, these values are achieved faster, leading to smaller values of t_1 and t_2 (Table 1). This observation is consistent with the dynamics of self-trapping of a narrow white light beam in the same system; an inverse relationship was found between optical intensity and time taken for the beam to self-trap.[2] This was because a critical change in refractive index was required to counter the diffraction of the beam (which was the same at all intensities) and achieve self-trapping. As a result, the spatial profile (diameter) of the self-trapped beam was essentially identical at all intensities.

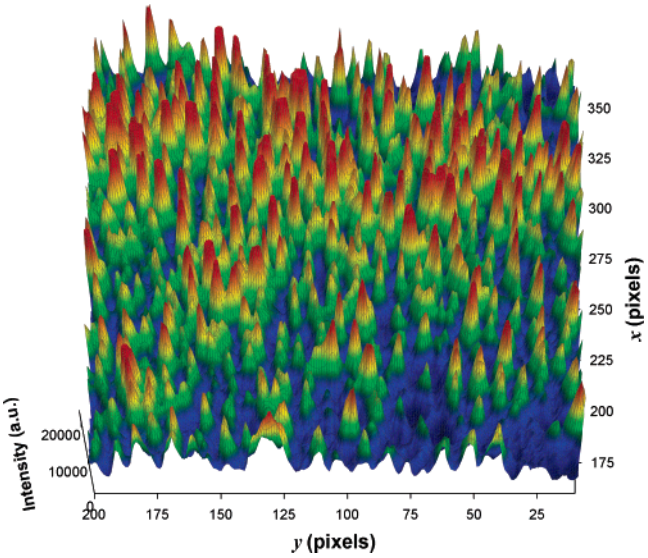

Figure 4. 3-D spatial intensity profile of white light after spontaneous formation of self-trapped filaments (bright spots) in an organosiloxane contained in an optically isotropic glass cuvette. The intensity profile was acquired at a propagation distance of 6.00 mm (1 pixel = 9.3 μm × 9.3 μm).

The power-dependent study of pattern formation showed that, despite differences in the rate of refractive index change, the broad beam always underwent two distinct transitions, first to self-trapped lamellae (once Δn_1 is achieved) and then to identical self-trapped filaments (once Δn_2 is achieved). After the second transition, light intensity is confined principally to the filaments. Refractive index changes within the filaments therefore continue to increase; however, the shape and spatial position of the filaments remained unchanged for as long as the system was monitored.

Random Intensity Perturbations in a Uniform Field. The power-dependent study showed that self-trapped filaments are the most stable form of white light propagation under the nonlinear conditions created by polymerization. It is then reasonable to anticipate that any spatial perturbation in intensity (and not only a 1-D periodic modulation) should seed the formation of filaments. To verify this, the birefringent polymethylmethacrylate cuvette was replaced with an optically isotropic glass one. Here, intensity perturbations originate only from random fluctuations in concentration or convection due to (exothermic) polymerization. Figure 4 is the 3-D beam intensity profile after spot formation at a propagation distance of 6.00 mm. Indeed, the beam transformed into multiple bright spots (each, the cross-section of a self-trapped filament) with an average diameter of 76 ± 5 μm (measured over an area of 2500 μm × 2500 μm over 28 experiments). This is in excellent agreement with the spot size measured in experiments with the birefringent cuvette (Table 2). In the latter case, however, the spots formed a closely spaced 2-D periodic array. Although closely packed, the bright spots in the glass cuvette were randomly positioned in space (Figure 4).

The glass cuvette experiment showed that any spatial modulation in intensity of the broad beam (and not only a 1-D

(37) Measurements made from the optical micrographs of the microstructured organosiloxane are approximate; this is due to surface inhomogeneities that develop when the sample is extracted from the cuvette and to shrinkage of the sample caused by condensation of residual silicon alkoxide and silanol groups upon exposure to atmospheric moisture.

(38) (a) Kewitsch, A.; Yariv, A. *Opt. Lett.* **1996**, *21*, 24−26. (b) Kewitsch, A.; Yariv, A. *Appl. Phys. Lett.* **1996**, *68*, 455−457.

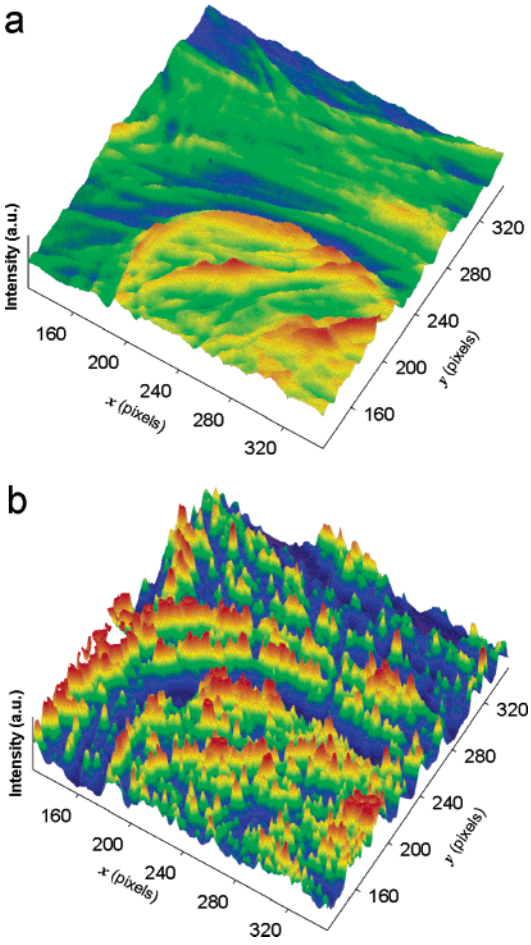

Figure 5. 3-D spatial intensity profiles of white light at 23 mW show that at approximately 140 s, convection lines are (a) amplified and after 270 s themselves transform into (b) individual self-trapped filaments due to photopolymerization in an organosiloxane contained in an optically isotropic glass cuvette.

periodic modulation) self-traps after a certain period of time, that is, once a critical index change (Δn_1) is achieved. With time (as the second critical index change Δn_2 is achieved), minor intensity variations within the self-trapped pattern itself become amplified and spontaneously transform into essentially identical self-trapped filaments. Another striking example of this property is shown in Figure 5a,b, which consists of 3-D intensity profiles of a high-power (23.0 mW) broad beam of white light. Rapid polymerization rates (and consequent rapid changes in the local concentration of the medium) at this power create convection currents in the fluid medium that introduce intensity variations across the beam. Figure 5a, which was acquired after 140 s of polymerization, shows that these variations amplified and self-trapped and (after 270 s) transformed into self-trapped filaments (Figure 5b). The filaments as a result are positioned along the fingerprint-like patterns created by convection currents.

Controlled Noise in a Uniform Field. By deliberately controlling noise in the broad beam, it was possible to achieve highly organized arrays of self-trapped filaments. A technique applied in experiments with partially coherent light[15] was employed; an amplitude mask placed at the entrance face of a glass cuvette imposed a highly periodic (80 μm) 1-D intensity modulation (along the x direction) of the broad white light beam.[39] The modulation was sufficiently weak that under linear conditions it could not be detected at a propagation distance of 6.00 mm. Figure 6 traces resulting changes to the beam intensity profile in the presence of polymerization at a propagation distance of 6.00 mm (the corresponding movie (MOVIE_S2.wmv) and temporal evolution of 1-D cross-sections (Figure S4) are presented as Supporting Information). Within 578 s, the beam transformed into a highly periodic 1-D array of bright stripes (Figure 6c); the periodicity of the stripes was measured (over an area of 2500 μm $\times$ 2500 μm and over seven experiments) to be 80 $\pm$ 3 μm, which corresponded to the periodicity (80 μm) of the 1-D intensity modulation imposed on the beam. The modulation depth of this pattern increased over the next 231 s (Figure 6c−e), during which minor intensity variations developed along each bright stripe, causing their transformation into individual bright spots (Figure 6e). The modulation depth of the spots then increased over time (Figure 6e−h), leading to a highly periodic 2-D array of bright spots. The width of each spot was measured (over an area of 2500 μm $\times$ 2500 μm and over four experiments) to be 66 $\pm$ 5 μm. Essentially the same value, 65 $\pm$ 6 μm (measured over 2500 μm $\times$ 2500 μm and over three experiments), was obtained when the 1-D modulation was applied in the y direction.

In fact, a comparison of spot sizes obtained in the different experiments listed in Table 2 shows that, regardless of the form of noise, the broad beam of white light always transformed into essentially identical filaments in the organosiloxane. However, the system was insensitive to any 1-D modulation with a length scale that was smaller than the average spot diameter. For example, a 1-D modulation with a periodicity of 20 μm led to the spontaneous formation of self-trapped filaments with random spatial positions (Figure S5, Supporting Information); the behavior of the beam in this system was similar to its behavior in a system without a 1-D intensity modulation (Figure 4).

Summary and Outlook

A uniform broad beam of white light spontaneously and collectively transformed into multiple self-trapped filaments in a photopolymerizable organosiloxane. Consistent with recently developed theoretical models, pattern formation in a broad white light beam occurred under the same conditions that cause self-trapping of a narrow white light beam. Regardless of optical power or the type of noise, pattern formation always led to essentially identical self-trapped filaments. Each filament is similar to a single self-trapped beam and represents the most stable form of light propagation under the nonlinear conditions created by photopolymerization.

Because photoinduced refractive index changes in the organosiloxane are permanent, optical micrographs of the irradiated sample showed microstructural changes that underlie pattern formation. Irradiated samples consisted of planar and channel waveguide arrays induced by self-trapped lamellae and self-trapped filaments of white light, respectively. The process is therefore a single-step, mask-free lithographic route to micro-periodic materials with advanced optical properties; 2-D arrays of channel waveguides (that are at least 6.00 cm long) have potential applications as efficient light-guiding systems such as

(39) The modulation periodicity was deliberately selected to correspond to the spacing of bright stripes observed in experiments carried out in the polymethylmethacrylate cuvette. The amplitude mask, however, imposed an intensity modulation that was strictly periodic over the entire beam.

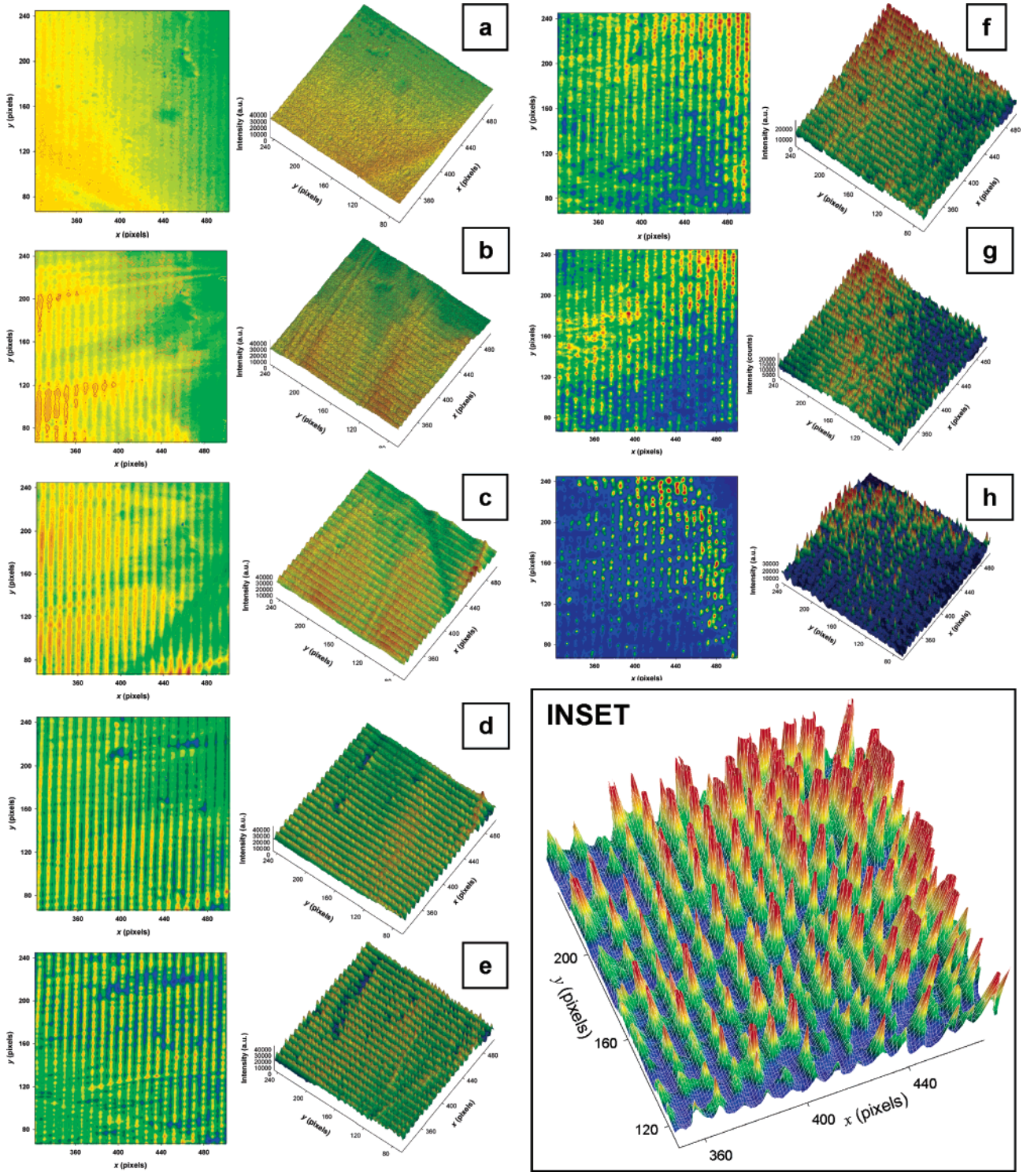

Figure 6. Temporal evolution of the 2-D and 3-D spatial intensity profiles of a uniform beam of white light with a 1-D periodic (80 μm) modulation (along *x*-axis) at a propagation distance of 6.00 mm in photopolymerizable organosiloxane contained in a glass cuvette at (a) 0 s, (b) 462 s, (c) 578 s, (d) 732 s, (e) 809 s, (f) 871 s, (g) 1040 s, and (h) 2163 s. The inset is a magnified intensity profile of individual self-trapped filaments of white light at 2163 s. For clarity, intensities were normalized to the maximum peak in images f−h (1 pixel = 9.3 μm × 9.3 μm). (The complete sequence of images is available as MovieS2, Supporting Information.)

artificial compound eyes[40] and photonic crystal (holey) fibers.[41] On the other hand, the formation of periodic patterns in an isotropic medium exposed to a uniform beam is unexpected and therefore significant in the synthesis and extensive applications of free-radical photopolymerizable materials. These observations are consistent with the formation of random patterns in thin photopolymerized films.[42] From a broader perspective, pattern formation caused by competition between diffraction and refraction of light under nonlinear conditions has parallels in a diverse range of physical systems, where two competing factors

(40) Jeong, K.-H.; Kim, J.; Lee, L. P. *Science* **2006**, *312*, 557−561.
(41) Russell, P. *Science* **2003**, *299*, 358−362.
(42) Streppel, U.; Dannberg, P.; Wächter, C.; Bräuer, A.; Kowarschik, R. *Appl. Opt.* **2003**, *42*, 3570−3579.

(e.g., diffusion−reaction) under nonequilibrium conditions also lead to the spontaneous formation of patterns.[43]

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Supporting Information Available: (1) Video of temporal evolution of beam intensity profiles during spontaneous pattern formation of organosiloxane in a polymethylmethacrylate cuvette (corresponding to Figure 1). (2) Video of temporal evolution of beam intensity profiles during spontaneous pattern formation of organosiloxane with an amplitude mask (periodicity = 80 μm, corresponding to Figure 6). (3) Experimental details. (4) Control experiments of the propagation of broad light beam in a non-photopolymerizable medium. (5) Temporal evolution of one-dimensional intensity profiles for spontaneous pattern formation with a polymethylmethacrylate cuvette (corresponding to Figure 1). (6) Temporal evolution of one-dimensional intensity profiles for spontaneous pattern formation with an amplitude mask (corresponding to Figure 6). (7) Spontaneous pattern formation with an amplitude mask with periodicity = 20 μm. This material is available free of charge via the Internet at http://pubs.acs.org.

JA068967B

(43) Ball, P. *The Self-Made Tapestry: Pattern Formation in Nature*; Oxford University Press: New York, 1998.