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Experimental investigation of long time irradiation in polydiene solutions: reversibility and instabilities

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Abstract
Polydiene solutions have recently been shown to possess a refractive index/concentration optical nonlinearity upon irradiation by CW-laser of a power as low as a few mW with typical timescales for solitonic formation in the order of seconds. Here we report on the effects of longer time laser irradiations which unveiled a variety of light-induced patterns. At extended irradiation times, rather than saturation or steady state of the single-filament pattern initially formed, the formation of more complex structures was systematically observed. The reversibility of the laser-induced concentration increase was shown to depend on irradiation time. Whereas exposures of the order of the inverse of the rate of formation resulted in reversible patterns, prolonged irradiation led to surprisingly long lasting irreversible structures that even resisted dissolution in a pure solvent. An intermediate case of semi-reversible patterns was observed giving rise to a pearl-necklace formation. Despite the as yet unidentified coupling, polydiene solutions offer a rich playground for soft matter nonlinear optics and potentially provide a readily available system for micro-patterning in a lithographic-like manner.

Keywords: laser micropatterning, polydiene solutions, soft matter, non linear optics, optical spatial, solitons, modulation instabilities

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Light-induced change of the refractive index can be triggered in many different materials through various mechanisms [1]. In particular a number of complex, often multi-constituent materials, belonging to the broad range of soft condensed matter, present refractive index nonlinearities. The best known case is certainly the colloidal particle dispersion, where the gradient of a laser electric field leads to a local increase of the number density of the colloids and an increase of the refractive index [2]. Other systems include photopolymers and their complex optical nonlinearities triggered by photo-induced chemical reactions [3]. Light-induced thermal diffusion (diffusion motions induced by a temperature gradient) may also be used to trigger spectacular optical effects and material patterning [4].

An intriguing case of a (nonlinear) time-dependent optical response was recently revealed in polydiene solutions in alkanes [5]. The transparent solutions were observed to pattern upon mild CW-laser irradiation ($P \sim$ mW). As has been reported, the light–matter coupling leads to the formation of patterns, such as optical spatial soliton-like filaments [6],

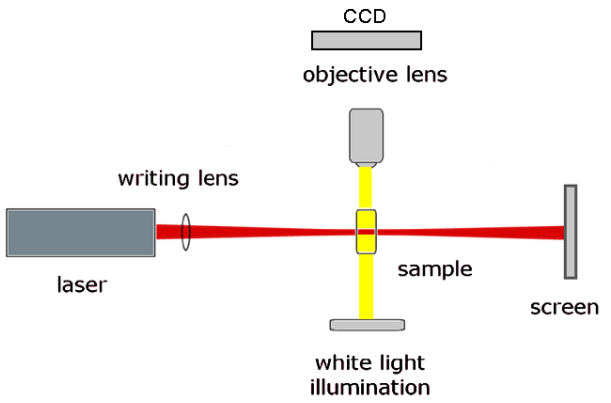

Figure 1. A schematic of the experimental setup for creating and simultaneously imaging the light-induced patterns. The laser beam is focused by a writing lens in the middle of the sample cell. The formed structures are imaged by the microscope objective lens, while the transmitted beam is imaged on a screen.

holographic gratings [7], 2D multi-filament periodic arrays and 3D multi-filament bundles [8, 9]. We here present further experimental results on patterning and mostly on the effect of longer time irradiation, revealing a broad range of complex patterns arising from various types of instabilities. Moreover, we established that long-lasting irreversible structures could form upon long irradiation times.

2. Materials and experiments

The samples consisted of *cis*-1,4 polybutadienes (PB) or *cis*-1,4 polyisoprenes (PB) from various sources with a molecular weight in the order of 390–1090 kg mol^{-1} dispersed in alkanes (good solvents for polydienes) with typical concentrations ranging from 5 to 50% polymer weight fraction. As required for the efficient light-material coupling, the solutions used were highly viscoelastic, i.e. combining a very large viscosity with a high rubbery elastic modulus. A CW-laser beam was focused in the sample cells as described elsewhere in more detail [9] and depicted in the sketch below (figure 1). The power was adjusted using neutral density filters. Two different lasers ($\lambda = 671$ nm, $P_{\max} = 300$ mW and $\lambda = 660$ nm, $P_{\max} = 150$ mW) were alternatively used in the reported experiments. The transmission pattern was observed projected on a screen; the material pattern created and the scattered laser light were imaged from a side view through an objective lens on a CCD camera. Imaging the pattern provided information on the formed refractive index changes and their time evolution and imaging of the scattered light revealed the path of the light. The transmission pattern provided information on the kinetics. The observed changes from a simple spot to much more complicated patterns revealed the complex evolution of the light transmission through the sample. The number of formed fibrils could often be deduced from the transmission pattern especially in the case of the modulation instabilities driven multi-fibril pattern.

3. Results and discussion

3.1. Long distance beam self-trapping

The optical nonlinearity in polydiene solutions in alkanes has been shown to be of the self-focusing type. Here we illustrate the ability to self-trap a beam over large distances (figure 2). A red laser beam (power $P = 29$ mW) was focused by a 16× (numerical aperture NA = 0.32) microscope lens (beam waist $\sim$ 10 μm) into a 5 mm × 5 mm × 25 mm square cell filled with a semidilute solution of PI/decane (molecular weight $M = 1090$ kg mol^{-1}, concentration $c = 6.6$ wt%). The scattered laser light scattering at an angle $\sim$90° was imaged on a CCD camera.

The diffraction of the focused laser beam is well imaged at the start of the experiment (figure 1(a)). After a few seconds of irradiation, the beam is clearly self-trapped over the whole image size cell length (5 mm in this case) into a single light filament (figure 1(b)) with a seemingly constant diameter of about 10 μm. As can be seen in figures 2(a) and (b), the self-focusing length in the order of a few millimeters largely exceeded the Rayleigh length of the incoming beam, which was in the order of 10 μm in this case.

Indeed lower magnification imaging revealed that the filament covered the whole cell length (5 mm in this case). The resulting change of the refractive index could also be imaged through phase contrast microscopy which confirmed the local increase of the refractive index. The resulting material patterning is also illustrated in figure 6.

Thanks to their large transmissions, polydiene solutions provide a rather unique case of self-focusing and material patterning over very large distances in soft matter where scattering or absorption losses usually limit self-propagation to relatively short distances.

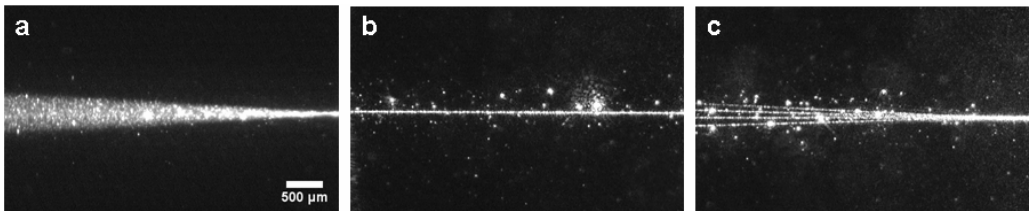

Figure 2. Solitonic formations in a PI/decane solution ($M = 1090$ kg mol^{-1}, $c = 6.6$ wt%). The laser beam ($P = 29$ mW) is focused through a spherical lens (NA = 0.32). (a) Spreading of the beam due to natural diffraction at $t = 0$ s, (b) Single optical spatial solitons formation as observed after a few minutes of irradiation. (c) Four fibril formation arising from optical instabilities. The beam propagation axis is from right to left.

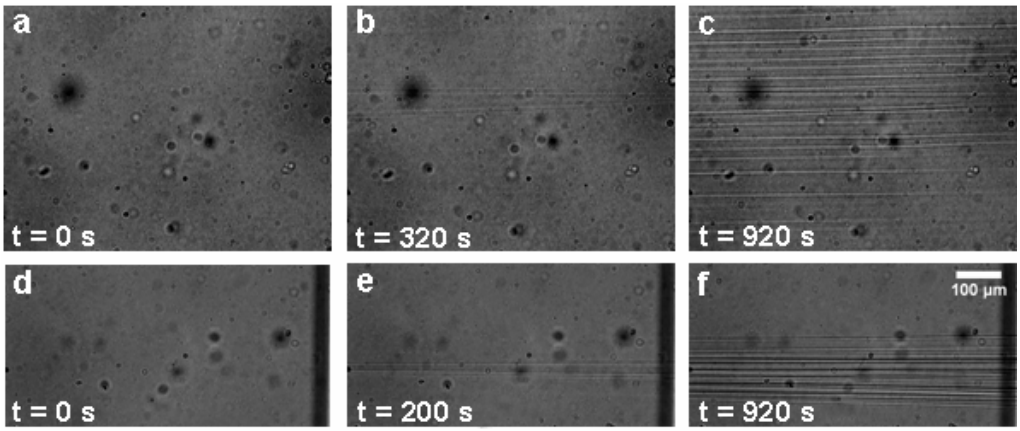

Figure 3. (a)–(c) 2D filament array formation obtained by a laser beam that is focused through a cylindrical lens ($f = 10$ mm) to form a sheet of light. (d)–(f) 3D multi-fiber bundle formation obtained by defocusing a spherical lens. The sample is a *cis*-1,4-PB/tetradecane solution ($M = 390$ kg mol^{-1}, $c = 14.7$ wt%) and the laser power is $P = 300$ mW.

3.2. Instabilities and pattern evolution

Two main types of pattern evolution were identified that gave rise to multi-fibril patterns: the 'distortion' of a single fibril into a many fibril pattern, and many fibrils from the start. The distinction is somewhat arbitrary; both can be combined, especially as the early modulational instabilities eventually gave rise to the later evolution. The proposed distinction conveys the important issue of kinetics in this non-instantaneous, asymmetric material where the decay time is much larger than the forming time.

3.2.1. Early instabilities. Self-trapped beams are prone to optical instabilities, where the small amplitude and phase perturbations (from noise) can grow rapidly. They are often referred to as modulation instabilities (MI) [10]. Some very clear evidence of the occurrence of MI in polydiene solutions is also shown in figure 1(c), where the same focused beam as in figure 2(b), but with a larger power (150 mW) gave rise to four fibrils roughly equally spaced in the initial light cone. These four fibrils grew through the whole 5 mm of the used cuvette.

We previously showed that large beams lead to multi-fibril patternings, providing a clear proof of the occurrence of modulational instabilities [9]. Here we look in more detail at the growth of the multi-fibril pattern when cylindrical or defocused spherical lenses are used.

The patterning using a cylindrical lens (focal length $f = 10$ mm) is shown in figure 3(a)–(c). After 15 min (figure 3(c)), a single array of ∼15 almost equally spaced and parallel lines is clearly imaged. A careful examination of the sequence revealed that not all the fibers appear simultaneously. The first visible fibrils became visible in the middle of the imaged area (where the intensity is higher) after 320 s of irradiation. The exterior fibrils became visible later on until the whole imaged area was filled with a regular 2D arrangement of filaments of a roughly constant diameter. The waveguiding from each fiber in the array could clearly be seen in the scattering image ($\theta = 90°$).

Very similar sequences were observed for the fiber bundles formed by a defocused spherical lens. A few central fibers appeared first at the beam center, followed by the more peripheral ones (figures 3(d) and (e)). The occurrence of multi-fibrils could also be seen through the evolution of the transmitted pattern as multiple bright spots became clearly visible.

Noticeably, each fibril in figure 3 appeared simultaneously along the propagation direction over the observed area (horizontal direction of the images). This was also the case for the single fibril formation (obtained with a tighter Gaussian beam) [9]. In the case of extended multi-fibril formations in larger cells as in figure 2(c), the individual fibrils were observed to self-propagate individually with sometimes different rates, possibly through self-focusing of the light transported in the formed wave guide.

The growth rates of the individual fibrils in the multi-fibril formation were much slower than the growth rate observed for a single filament in a tight focus with the same power (12 s for the illustrated case) [9, 11]. Typically, whereas the first fibers become visible at around 320 s, similar experiments would lead to visible fibers in only a few seconds. To obtain such a slow rate, a low laser power would be needed.

3.2.2. Later stage secondary formations. Single fibril patterns were observed to form using a 5× objective as a writing lens [9]. As reported elsewhere, the rate of increase of the refractive index for such an individual fibril typically ranged from a few (s)$^{-1}$ to (100 s)$^{-1}$ [9, 11] depending on the sample conditions. Noticeably these rates were found to be inversely proportional to the laser power. Here we report on observations on a timescale much larger than 1/rate. We observed that the single straight fibrils were not stable up to prolonged irradiation, as they were systematically found to evolve towards more complex patterns.

Typical examples of the distortion of the single fibril patterns created by irradiation with a focused laser beam (figures 4(a) and (c)) as a result of prolonged irradiation are shown in the phase contrast images of figure 4. In figure 4, the initially straight structure (a) was observed to twist (b). In a parent solution, the occurrence of multi-fibrilar (three

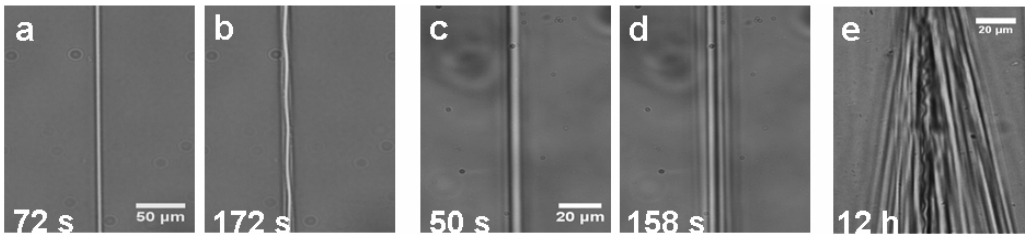

Figure 4. Evolution of the single fibril pattern obtained with a focused lens (beam waist diameter $\sim 20\ \mu$m); (a) and (b) Formation of a single fiber (after $t = 72$ s of irradiation) which is twisted after $t = 172$ s, formed in a *cis*-1,4 PI/decane solution ($M = 1090$ kg mol^{-1}, $c = 5.6$ wt%); (c) and (d) Single fiber pattern that eventually changes to a multi-fibrilar complex structure. The solution is *cis*-1,4 PI/decane ($M = 1090$ kg mol^{-1}, $c = 9.51$ wt%). (e) Extended multi-fiber structure after 12 h of irradiation of a *cis*-1,4 PI/tetradecane solution ($M = 1090$ kg mol^{-1}, $c = 18.58$ wt%).

fibrils) formation (figure 4(d)) is shown after a similar time. At much longer irradiations, a complex multi-fibril structure was observed with broad transverse dimension that could eventually exceed the laser beam waist (figure 4(e)). It is worth noticing the presence of the twisted fibril in the middle of the structure, very reminiscent of figure 4(b).

It is worth noticing that the reproducibility of the sequence of secondary pattern formations was difficult to establish as different types of secondary structure could form in otherwise very similar conditions. Both optical and possibly mechanical instabilities present in the material (i.e. flow in the solution) could contribute to the formation of the secondary structures. However, very long irradiation systematically ended up with a complex multi-fibril pattern like the one depicted in figure 4(e).

Though best seen through phase imaging, the evolution of the single-fibril patterns could also be inferred from the observation of the laser transmission pattern [5]. It first showed the usual rapid evolution with dynamic concentric diffraction rings, which was followed by a strong slowdown. However the pattern did not freeze totally but smaller secondary patterns were observed with the characteristic evolution, on top of the almost frozen parts corresponding to the initial formation. Patterns like the one in figure 4(e) had, as could be expected from their structure, complex transmission patterns.

3.3. Reversibility

3.3.1. Reversible and semi-reversible patterns. Owing to the solution nature of the material, the concentration gradients forming the patterns should have been expected to relax due to osmotic forces, with a timescale comparable to the formation time scale after the irradiation was stopped. However, very long-living structures were noticed and their extremely slow evolution motivated a careful study of the re-solubility of the formed fibers in the surrounding solution by video microscopy.

The evolutions of the written patterns after stopping the laser irradiation were found to depend on both the properties of the polydiene solutions and on the irradiation conditions. For irradiation times of the order of the inverse of the formation rate, single fibers formed at the focus of the spherical lens were observed to disappear from the phase image. However, the time for dissolution was much slower than for formation. For prolonged irradiation (typically larger than 10/(formation rate)), the formed structure remained visible up to very long times, as long as months for structures written in tens of seconds.

Interestingly, an intermediate regime could be identified, where a break-up of the original fibril was observed. Figure 5 displays a series of microscope images of a fiber formed in a PI ($M = 378$ kg mol^{-1})/decane solution ($c = 9.51$ wt%) after 45 s of irradiation ($P = 238$ mW). The first image ($t = 0$ s) was captured directly after switching off the laser light, while the other images correspond to later times: a downwards bend of the fiber (300 s after stopping the laser) was first seen (figure 5(b)) and was attributed to gravity as the density of the polymer is higher than the density of the solvent and therefore the pattern is denser than the surrounding medium. Then (after about 400 s), the fiber eventually showed visible inhomogeneities in the radial dimension with alternating thinner and broader regions along the laser propagation direction, (figures 5(c) and (d)). Later break-up in the thinner regions and retraction of the swollen pieces resulted in isolated globular structures (figure 5(e)). Noticeably, the dots appeared to conserve a spatial correlation even after break-up, as their eventual up and down motions (created by gravity or bubble motion) were clearly in a correlated fashion. One possible explanation is that thin sub-micron threads not resolved by optical microscopy connect the dots. At much later stages (not shown here) the dot-like structures appear to be almost uniform in size (roughly 5 μm) and insoluble in the surrounding solution.

This break-up was seen for the less viscous solutions and for solutions with very high viscosities, fibers which maintained their integrity were not seen. This points out the importance of the mechanical properties of the medium in the stability of the pattern.

3.3.2. Insoluble fiber bundles. The formation of long-living structures formed pointed towards the enhanced stability of the patterned material. In order to check possibilities of formation of irreversible structures, we performed solvent rinsing experiments. Fibril bundles were used rather than single fibrils, as they were easier to manipulate.

Dense fibril bundles were produced by hours of irradiation (typically overnight) with a defocused 5× lens. After patterning, the whole glass cell was immersed in a large pot filled with pure hexane, which is a good solvent for the polymer. After 4 h, the cell cover was gently removed, and the

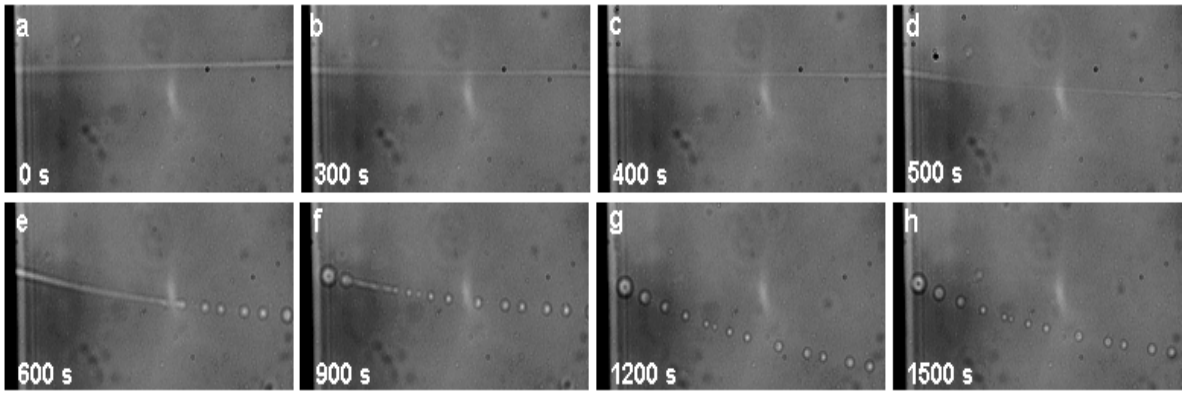

Figure 5. Microscope images of the fiber decay process at different times after switching off the laser beam. The fiber was formed after irradiating a PI ($M = 378$ kg mol^{-1})/decane solution ($c = 9.51$ wt%) for 45 s ($P = 238$ mW) corresponding to a formation rate 1/20s.

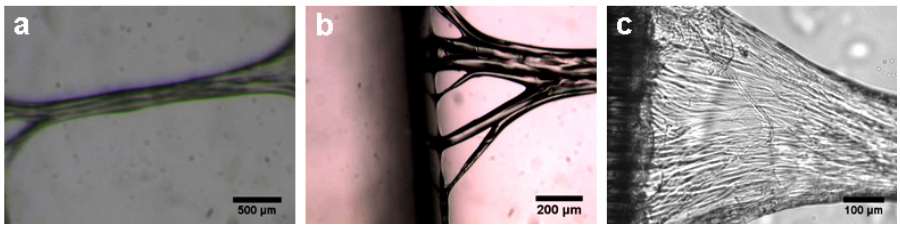

Figure 6. Microscope image from a dry fiber bundle formed by prolonged irradiation of a *cis*-1,4 PB/tetradecane solution ($c = 14.7$ wt%) (a)). The whole cell is imaged (2 mm long). (b) Magnified image of the bundle end attached to the glass cell window. (c) Phase contrast image of a PB multi-bundle immersed in pure solvent.

rinsing operation was repeated 3–4 times. A polymer structure could clearly be seen with the naked eye, sticking between the walls of the rinsed glass cell. The cell was thereafter put in a vacuum oven for 3 h, to insure the evaporation of the remaining solvent leaving a dry polymer bundle. Typical images of such a rinsed and solvent re-swollen bundle are shown in figure 6.

The presence of such a structure despite the prolonged exposure to hexane clearly proved its insolubility in hexane, a good solvent for the original polymer. This surprising insolubility is illustrated in figure 6(c), where the bundle is imaged re-swollen in hexane. Such a resistance to the solvent could only result from the presence of some kind of 'crosslinks' created upon irradiation. The type of modification leading to such a stability is not clear and the possibilities will be discussed in the next part.

The specific structure certainly occurred as a result of the collapse of the different fibrils of the bundle during the rinsing process. The presence of the individual fibrils could still be seen, as they appeared not totally fused. The irradiated polymer was efficiently stuck to the glass wall of the cell. It is worth noticing that only relatively large structures remained unaffected by the treatment. Smaller bundles or even single fibrils were not re-dissolved by the hexane, but were much more difficult to isolate as they did not remain attached to the glass cell walls. Some of these smaller structures could however be seen in the rinsing hexane.

A nice confirmation of very stable patterning over long distances was obtained by using the self-trapped beam to prepare long filaments. A multi-fiber pattern (probably consisting of several fibers arranged into a bundle) was written along the axis of a 3 cm long glass cuvette in a solution of *cis*-1,4 PI ($M = 1090$ kg mol^{-1})/decane, at $c = 6.6$ wt%. Laser irradiation resulted in a long structure, extending between the bottom of the cell and the solution meniscus (∼2.5 cm). The gravity-induced very slow sedimentation of the long multi-fiber, followed by video microscopy as shown in figure 7, demonstrated the very long permanent pattern.

The buckling of the fiber bundle apparent in figure 7 reflects the enhanced mechanical stability of the bundle structure and was reminiscent of the buckling of an elastic filament. The characteristic length of the buckled structure should relate to a mechanical persistence length. At the end of the process, a thick layer of insoluble fibers was formed at the bottom of the cuvette.

3.4. Discussion

Several self-focusing nonlinearities have been reported in soft matter, that may give rise to self-guiding and optical spatial solitons (OSS) [12], when the self-lensing exactly balances the broadening of the beam due to diffraction. In binary mixtures, the local increase of the refractive index providing the self-lensing may arise from local variations in the concentration of the constituents and self-trapped beams may lead to the formation of filament-like matter patterns of constant transverse dimensions.

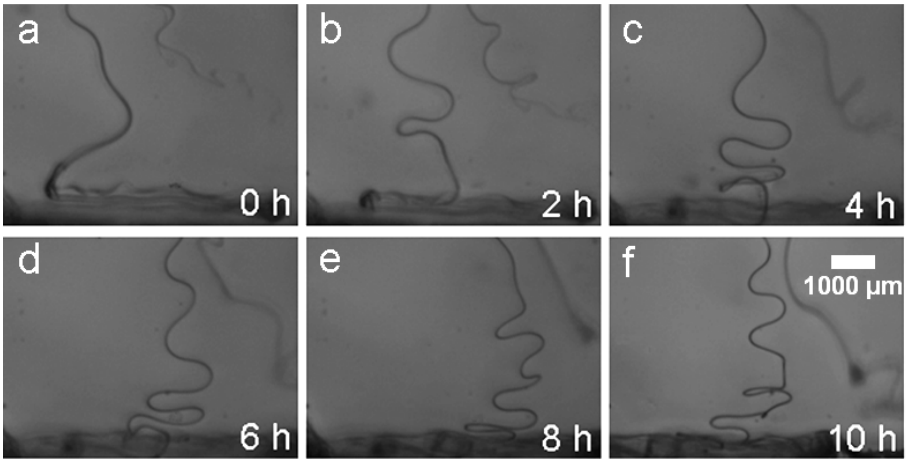

Figure 7. Microscope images of a long fiber bundled upon sedimentation. The bundle was formed after the prolonged irradiation of a *cis*-1,4 PI ($M = 1090$ kg mol^{-1})/decane solution ($c = 6.6$ wt%), and its length was about 2.5 cm. After formation, the sample cell was placed vertically to allow sedimentation of the written structure due to gravity.

The various observations described above provide an experimental demonstration of the complex light-driven patterning achievable in polydiene solutions. They represent a clear manifestation of the patterning of soft matter through nonlinear optics. To us, they certainly lie among the most remarkable and versatile experimental demonstrations of beam self-trapping and the instabilities induced by concentration changes in mixtures, even though the precise light-material coupling leading to the local increase of the concentration is still not identified. This lack hinders the development of a full modeling. Such a model could lead to a quantitative description and allow theoretical predictions of the various patterning and will certainly help to make our study somewhat more quantitative. However, we believe that by exploring the different possibilities offered by the material and establishing a clear phenomenology, we will progress towards this modelization. It allows categorization of the optical nonlinearity and the identification of relevant parameters.

Based on the observations, polydiene solutions should range into the category of non-instantaneous, non-local and saturable nonlinear materials. Those specific properties are present in other materials like photopolymers [3, 13] where they give rise to various complex instabilities and subsequent patterning. Cases of irreversible nonlinearity where permanent material patterns may be obtained have received attention [6, 14]. However, the phenomenology and the type of instabilities that we reported seem qualitatively different from those present in other materials.

On top of the interest in nonlinear optics, polydiene solutions may offer interesting patterning possibilities. Complex patterns of solitonic fibrils emerge through instabilities. Their slow decay allows us to freeze the patterns in the absence of irradiation. Noticeably, the patterns are all made of fibrils with width $\sim$10 μm, which appeared to be imposed by the optical field and roughly independent of the precise material and illumination conditions. Moreover, the light-driven increase of the concentration produces local crosslinks that eventually prevent the re-dissolution of the formed patterns.

The interesting case of the semi-reversible formation leading to the formation of insoluble equally spaced spheroids seems intermediate between the fully crosslinked and the fully reversible formations. This remarkable formation could be due to an underlying longitudinal structure in the single filament, with a variation of the concentration and/or of the crosslink density along the direction of propagation. The presence of crosslink variation along single lines could be inferred from the semi-reversible cases. It could originate from optically induced instabilities. This type of pearl necklace longitudinal variation has often been predicted if not observed in a number of SM nonlinear optic systems [14, 15]. However it was not really possible to discern longitudinal refractive index variation by the used phase contrast imaging setup. Similarly, a longitudinal variation of the crosslink density could also be responsible for the opto-mechanically driven distortions as it might become self-amplified (i.e. twisting). In addition, there is a possibility of stress induced by the local crosslink variation which leads to a mechanical distortion of the straight fibers.

The nature of the crosslinking points is not yet established. Different possibilities arise such as the formation of chemical crosslinks leading to the formation of a rubber. However, the stability of the chemical bound and the low light level used seem to be enough to exclude this type of mechanism. A physical crosslink could also explain the irreversibility. The presence of micro-crystallites, where locally the polymer chains arrange on a crystalline lattice, would provide a barrier to re-dissolution. Indeed polyisoprene and polybutadiene are known to be able to crystallize for example under mechanical stress [16, 17]. However, preliminary x-ray diffraction on the rinsed bundles does not seem to show a large amount of crystallization.

The permanent material modification, turning the very viscous polymer melts or solutions into an elastic rubber, could turn out to be very useful. It could be used in a lithographic-like approach to optically design and produce micro-patterned rubber. It may offer a simple way for creating long lasting structures in polymer solutions in analogy to lithographic [18] and photopolymerization [19] approaches, however, owing to a different effect.

4. Concluding remarks

Polydiene solutions behave as photorefractive polymer solutions. The unexpected response of the transparent solutions to an applied optical field lead to a variety of patterns made of solitonic fibrils. The single fibril formation was not stable over a long time. The single self-trapped beam was systematically observed to evolve into the formation of more complex structures. Though the evolution of the patterns may have depended on specific conditions, a very long irradiation (many hours) invariably led to complex multi-fibrils patterns.

The reversibility of the peculiar laser-induced matter organization was found to depend on the irradiation time. For irradiation times comparable to the inverse of the formation rate, written structures of higher polymer concentration re-dissolved in the solutions, while more prolonged irradiation resulted in insoluble patterns.

Despite the unidentified coupling between the optical field and the local concentration of the polymer solutions, polydiene solutions emerge as an unexpected and accessible material platform for experiments in the rapidly growing field of soft matter nonlinear optics. Moreover, the long time stability of structures obtained after the prolonged irradiation of highly viscous solutions could potentially open the possibility of utilizing polydiene solutions as a cheap material for lithography. The polymer-based materials could take advantage of the well established polydiene chemistry [20], which allows the synthesis of a large variety of molecular architecture, definitely offering several perspectives for development of new photopolymers.

Acknowledgments

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