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Cite as: AIP Conference Proceedings **1288**, 123 (2010); https://doi.org/10.1063/1.3521342
Published Online: 15 November 2010

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Polydiene Solutions: A Surprising Versatile Non Linear Optics Material

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Abstract. The astonishing non linear optical properties of solutions of polyisoprene and polybutadiene in various organic solvents are reviewed: When irradiated with mild laser light, the non absorbing solutions respond by a change of the local polymer concentration inducing a local variation of the refractive index that alters the light propagation. Observed formations include optical spatial soliton-like filaments, multi-filaments arrays resulting from modulational instabilities, multi-filament holographic gratings or even more complex structures.
Keywords: polydienes solutions, non linear optics, soft matter, optical spatial solitons, modulational instabilities.

PACS: 42.65.Jx

INTRODUCTION

Coupling between light and matter gives rise to a number of optical non linearities[1]. In Soft Matter systems, which are characterized by the presence of mesoscopic length scales, the coupling of the optical excitation with the mesoscopic degree of freedom may generate optical non linearities and result in the formation of spectacular light propagation and material patterns. Examples are the self guiding observed in nematic liquid crystals[2], and in colloidal solutions[3]. Such coupling and non-linearities are not expected in transparent polymer solutions. However, an unexpected coupling of light and polymer concentration in binary solutions of polydienes dispersed in various organic solvents has recently been reported in a series of papers[4-6]. We will here briefly review the intriguing findings.

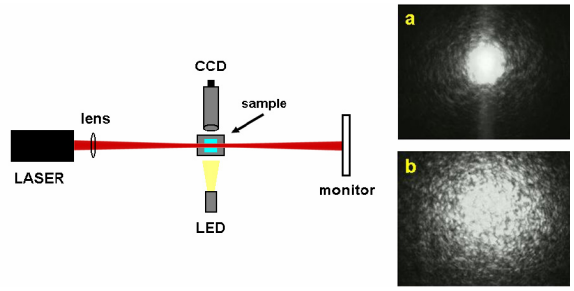

FIGURE 1. Schematic of the simple transmission experiments and image of the initial well-defined Gaussian spot of the transmitted beam projected on the screen(a) and its later appearance with a broader speckle-like pattern (b).

CP1288, *Emerging Trends and Novel Materials in Photonics, International Commission for Optics Topical Meeting*
edited by N. A. Vainos, S. Pissadakis, S. Couris, E. Paspalakis, and I. Koutselas

LASER WRITING IN POLYDIENE SOLUTIONS

The Transmission Experiments

The first hint into the existence of the light-material coupling was gained through a simple experiment where a laser beam with relatively low power (P<100mW) was focused into a solution by a 10 cm lens[4]. The transmitted beam projected on a screen was unexpectedly seen to undergo concentric evolution and broadening. (Fig. 1). The origin of the spectacular evolution could be attributed to the formation of a microscopic pattern along the propagation axis observed by microscopy, which evolved with time.

Material Conditions

Up to now, pattern formations have been observed in polydienes dispersed in various organic solvents. A required specificity for the active material seems to be the presence of the C=C double bond along the main chain backbone. Remarkably, materials based on isomers were the double bond is present on the side groups were not found active (Fig. 2). It is worth noticing that the reported active polymers polyisoprene (PI) and polybutadiene (PB) are the most common natural (PI) and synthetic rubbery (PB) materials.

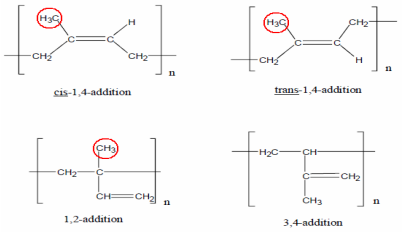

FIGURE 2. The different microstructures of the most common polydienes poly (isoprene) (R = CH3) and polybutadiene (R=H). The effect is observed for solutions of the 1, 4 addition (both cis and trans) but not of the 1, 2 addition

Using polymers of varying degrees of polymerization (molecular weight), Sigel et al[4]. identified a minimum concentration c_c below which no effect was observable.

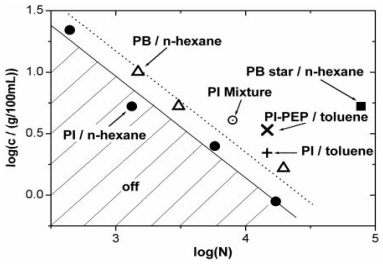

FIGURE 3. ON/OFF Concentration / degree of polymerization N diagram. Points correspond minimum concentration c_c to observe changes in the transmitted. Solid line and circles: PI/hexane, Dotted line and triangles: PB/ hexane . "PI mixture": mixture of a low N (1910) and high N (17060) PI in hexane

The value of this cutoff concentration appeared to be insensitive to laser irradiation power, but to depend on the degree of polymerization N as $c_c \sim N^{-0.8}$. The same scaling was observed for both PI and PB in hexane. This relationship resembles that of the overlap concentration c^* where individual macromolecules start to overlap substantially with each others. The value c_c was found to be in the range of the entanglement concentration (~10 c*) where solutions become strongly viscoelastic.

Filaments, Bundles and Holographic Gratings

Complementary to the transmission experiments, phase contrast microscopy was utilized to image the patterns and their formations[6, 7]. The formation of a single fiber like structure homogeneous over the full imaged area (0.5

mm~ focal depth, typically placed in the middle of the sample cell) was observed. The structure appeared to have a constant radius and a contrast increasing with time (Fig 4). The increasing contrast was attributed to a local increase of refractive index, itself attributed to a local increase of polymer concentration. This was confirmed by the observed tendency of the pattern to sink due to gravity.

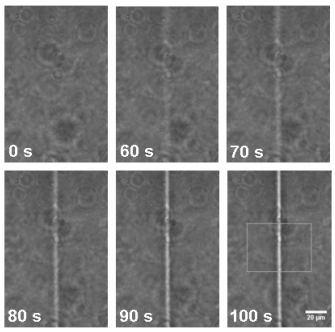

FIGURE 4. Typical time series of phase contrast images viewing the fiber formation. Material cis-1, 4 PB / tetradecane solution, at concentration c = 14.7 % wt, laser P = 238 mW. Starting from a transparent solution with no visible pattern, a region of higher intensity (larger phase gradient) appears in the image along the propagation of the laser beam

Interestingly, the use of a beam of larger dimension obtained by defocusing the lens or with a larger beam waist was not found to lead to one fiber with larger radial dimension but rather to a multi-fiber assembly where every fiber has a radial dimension very similar to the single filament formed with narrower waist. Similarly, applying a light sheet irradiation using a cylindrical lens also resulted in multi-fiber formations, as an array of equally spaced fibers was observed[6, 7].

The multi-fiber pattern is reminiscent of the instabilities induced by small phase and amplitude perturbations predicted and observed in a number of optical non linear system and in particular self focusing materials[8, 9].(Modulational Instabilities).

The irradiation by intensity gratings created by two crossing beams was shown to lead to the creation of optical gratings that could reach high efficiency[5]. It is now clear that the gratings consisted on layers of filament in the region of high intensities alternating with layers of unwritten material in the region of low light intensity. The formation time was found to be of the order of seconds to minutes depending of the conditions.

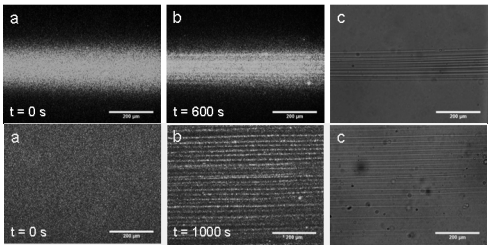

FIGURE 5. 3D fiber bundle (top) and 2D filament array (bottom) formation in a cis-1, 4 PB / tetradecane solution (M_w = 390 kg / mol, c = 14.7 % wt). A 300mW laser beam is passing through a defocused spherical lens (f = 35 mm) to form broad light beam or cylindrical lens (f = 10 mm) to form a light sheet. a) the initial beam, b) waveguiding of the beam through the (2+1)D (top) (1+1)D Bottom OSS filaments formed seen through the scattered light and c) phase image

Kinetics of Formation

Real time quantitative phase contrast microscopy allowed visualization and quantification of the refractive index changes. A detailed study of the kinetics of formation of the single filament in alkane solutions was achieved[6, 7, 10]. In an early stage, the imaged contrast was found to increase exponentially with time, in most of the explored conditions. Larger laser power leaded to faster rate $\Gamma \sim P$. The influence of the samples parameter were found to be more intricate with in particular no clear trend for concentration changes and a clear speeding up with increasing degree of polymerization[6, 7, 10].

In a later stage of the formation process, the kinetics seemed to slow down and the patterns appeared to be subjected to different type of instabilities, often giving rise to the formation of secondary patterns[7].

Discussion

Despite the well established phenomenology, the microscopic origin of the light-concentration coupling in the dispersions has, somewhat surprisingly, not yet been clarified. The mechanisms known to be effective in other soft matter systems, namely electrostrictive force in colloidal solutions, thermal diffusion and phase separation in pre-critical polymer solutions or molecular Kerr effect in liquid crystals are not expected to lead to any measurable variation of refractive index or concentration in these solutions[7]. The expected coupling parameters are small and compensated by the low osmotic compressibility. The low polarizability (weak optical forces) is confirmed by the low level of Rayleigh scattering. The absorption is also very low and moreover, the observed increase of polymer concentration in the irradiated region is at odd with the decrease expected in the case of a positive temperature gradient[7]. Moreover, none of this can account for the specificity of the active polydienes, especially the difference between the 1,2 and 1,4 isomers.

Beside the origin of the effect, a number of points remain to be clarified, like possible material modifications beside the increase of concentration, the reversibility of pattern formation with very long apparent stability.

CONCLUSION

Polydienes dispersions, based on easily available and easy to handle materials provide a unique example of laser-matter interaction. Though not fully understood, they offer a rich playground for non linear optics and 3D micropatterning.

ACKNOWLEDGMENTS

The Greek GSRT (PENED-03ED805) and the Max Planck Society (program IMPRS for polymer materials) are acknowledged for the financial support.

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