Self-induced transparency in diblock copolymer dispersions

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We report on the versatile effect of weak red laser light impinging on diblock copolymer [poly(isoprene-*b*-styrene)] dispersions in two selective solvents for each block. In the strongly scattering but transparent micellar solutions in hexane (a good solvent for polyisoprene), higher refractive index copolymer-rich fibers were formed. In the turbid dispersions of the same copolymer in ethyl acetate (a good solvent for polystyrene), the effect of self-induced transparency was observed. A two-step patterning mechanism caused the generation of a transparent microchannel, increasing light transmission. The analogy between the current effect and that observed in homopolymer polyisoprene solutions in different solvents is discussed toward an understanding of the unanticipated light–soft-matter interaction.   © 2012 Optical Society of America
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Recently, the manipulation of complex fluids by optical fields has attracted strong interest [1–3]. The best example is the manipulation of colloids with laser tweezers making use of radiation pressure [4]. Another widespread case is the optically induced thermophoresis of soft and biological matter where thermal gradients are generated by tightly focused laser beams [5,6]. In such multicomponent media, light–refractive-index couplings can arise at the mesoscopic level through molecular orientation and/or local solute concentration alterations. These material changes can be present in transparent media (nonresonant effects) and can give rise to various optical effects, like self-focusing or defocusing nonlinearities, as observed in colloidal dispersions [7]. Self-induced transparency (SIT) can also occur for an optically turbid starting material where the action of the laser induces light propagation.

The recent advances in material chemistry provide access to a wide range of systems with precise molecular structure and controlled interactions [8] opening ways for optical manipulation. However, only a few have been investigated so far [9]. An unanticipated light–soft-matter coupling was discovered in mixtures of organic solvents with common polymers, namely, *cis*-1,4-polyisoprene (PI) and *cis*-1,4-polybutadiene (PB). When irradiated with mild (intensity as low as $I \sim 1.6 \times 10^5$ W/m^2) laser light, the nonabsorbing transparent media responded by a local polymer concentration increase, which led to the formation of fibers [10]. This novel light–soft-matter interaction gave rise to numerous micropatterns. Depending on the irradiation conditions [11], optical spatial solitonlike filaments [7], multifilament arrays [12], and gratings [13] resulting from modulational instabilities [14] were formed. Very recently, a laser-induced local refractive index decrease was reported on such solutions [15]. This reverse material response indicated a nonelectrostrictive light–matter coupling.

This effect has been reported for polymers of various architectures, i.e., block copolymers, where a block of a polymer is covalently linked to a block of a chemically dissimilar polymer [10]. The required condition was that one of the blocks was PI or PB. Block copolymers offer a convenient way to access numerous morphologies, leading to different material properties. In particular, the amount of scattering can be enhanced by dispersing block copolymers in selective solvents, where self-assembly leads to sterically stabilized soft colloidal particles. The precise size and geometry of the formed structures depends on the molecular architecture, differences in solubility of the blocks, or even the preparation route. Thus, self-assemblies of various shapes and sizes, like micelles and vesicles, can be formed [16].

Here, we report on the optical response of such "colloidal" PI-based copolymer dispersions in two different solvents with varying solubility and selectivity. We show a unique case of SIT in the case of turbid dispersions, as a consequence of the light–polymer coupling and the metastable turbidity.

The response of the dispersions to laser exposure was observed through phase contrast microscopy where the sample was in a square cell (1 mm) mounted on the stage of a microscope slightly defocused to increase phase contrast (Fig. 1) [17]. An optical filter was used to block the scattered laser light. Dispersions of an asymmetric poly(isoprene-*b*-styrene) diblock copolymer [18] (IS, molecular weight $M = 424$ kg/mol, 75 wt. % isoprene) in hexane and ethyl acetate were irradiated with a 660 nm laser (linearly polarized in the y–z plane, maximum power $P = 45$ mW) focused by a microlens in the middle of the cell (beam diameter ∼20 μm at the focal point).

Hexane is a good athermal solvent for PI and a nonsolvent for PS. Poly(isoprene-*b*-styrene) in hexane forms starlike micelles with a PS core and a solvent-swollen PI corona [19], which sterically stabilizes the micelle,
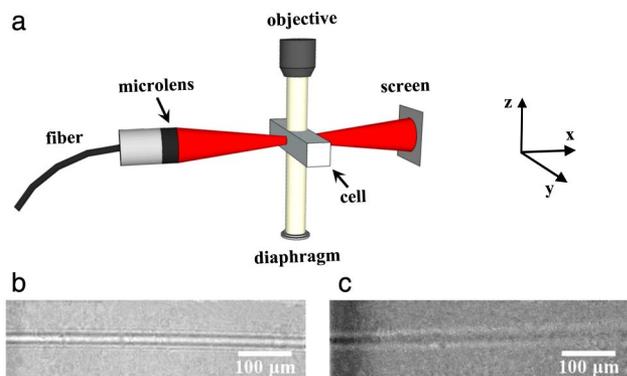
Fig. 1. (Color online) a, experimental setup; b, fiber formation ($I = 2 \times 10^7$ W/m^2) in a transparent (isoprene-b-styrene) diblock copolymer (IS) dispersion in hexane ($c = 0.037$ g/ml) consisting of starlike micelles with PS core and PI corona. The dispersion and the fiber display a positive optical contrast and a local refractive index increase, respectively. c, formation ($I = 3 \times 10^7$ W/m^2) of a polymer-depleted stripe (local refractive index decrease) in an IS/ethyl acetate dispersion ($c = 0.049$ g/ml) with positive contrast.

thereby preventing further aggregation. Their size was estimated through the hydrodynamic radius $R_h = 153$ nm. The large refractive index difference between polymer and solvent and the large micellar size resulted in strong light scattering for the dispersions at 5 wt. % (with a slightly white appearance). At room temperature (RT), ethyl acetate is a marginal solvent for PS and a bad solvent for PI, resulting in more complex dispersions. Depending on the preparation route, a dispersion of the same composition could lead to a material with different turbidity at RT. When mixed at RT, the dispersion was highly turbid but became transparent if heated to 40 °C for a few seconds and remained clear after cooling back to RT. Specific solvent–polymer-block interactions can be responsible for structural changes [20]. Micrometer-sized metastable aggregates are assumed to be at the origin of the turbidity [for 1 mm thick samples with a concentration $c = 0.049$ g/ml, transmission (Tr) is 40%]. For the heated clear dispersions, $R_h = 9$ nm. While the precise morphology remains to be fully characterized, the turbidity was found to be very reproducible.

Laser irradiation ($I = 2 \times 10^7$ W/m^2) of the hexane dispersions led to a fiberlike (Fig. 1b) local increase of the refractive index. It is attributed to a polymer concentration increase, since hexane possesses a lower refractive index ($n_{hex} = 1.375$) than the IS copolymer ($n_{IS} \sim 1.54$). The response is similar to that of homopolymer PI/hexane solutions [12]. It appears to be driven by the PI, whereas the specific micellar structure has a minor effect.

Irradiation ($I = 3 \times 10^7$ W/m^2) of the heated transparent IS/ethyl acetate dispersions led to a local refractive index decrease (Fig. 1c). It is attributed to a local polymer concentration decrease, since the refractive index of ethyl acetate ($n_{EA} = 1.372$) is also lower than n_{IS}. This response, opposite to the IS/hexane dispersions, is similar to that observed in homopolymer PI/tetrahydrofuran solutions [15]. The observed local refractive index
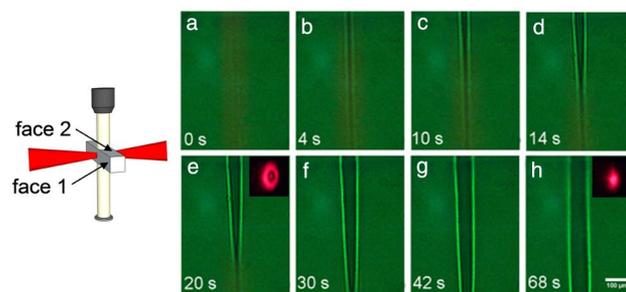
Fig. 2. (Color online) SIT in turbid copolymer dispersions. a–h, real-time phase contrast imaging of a turbid IS/ethyl acetate dispersion ($c = 0.049$ g/ml) through face 2 of the cell while the laser impinges the cell normal to face 1. After the rapid formation of a low refractive index stripe (a, b), a wide channel of increased transparency propagates (c–g) and finally covers the whole field of view (h). The irradiation time is indicated. The two insets show the transmitted laser spot.

decrease excludes a solely electrostrictive mechanism as an explanation [15].

Irradiation of the turbid IS/ethyl acetate dispersions revealed a different two-step process. A lower refractive index stripe rapidly appeared across the cell (Fig. 2a), similarly to the transparent IS/ethyl acetate dispersions. However, it was followed by a second process, where a narrow conical front propagated along the beam propagation direction (Fig. 2, top to bottom). It resulted in a tubular channel, which further broadened (Figs. 2c–2g) and eventually spread over the entire cell (Fig. 2h). This channel formation was accompanied by an increase of the light transmission and changes in the shape of the transmitted beam. The transmitted beam initially appeared as a weak Gaussian spot, which turned into a characteristic doughnut-shaped beam with a central bright spot, and finally transformed to a Gaussian-like beam with a high transmittance of Tr ∼ 0.9. Lower intensities led to similar patterns but slower kinetics. The long-time transmission remained steady in all cases.

SIT could also be observed in larger cells with light path lengths of 5 and 10 mm. The final Tr was again ∼0.9, reached at longer times because the front had to propagate further. Since the starting transmission was low (Tr < 0.1), this finding is a clear demonstration of SIT and self-propagation as the cell width was much larger than the beam Rayleigh length or the light mean free path for the turbid dispersions.

The optically "drilled" hole remained after laser switching-off. The bright spot in Fig. 3b shows the transmission of the microscope's white light through the formed channel, while the nonirradiated surrounding turbid liquid appears as a darker background. This proved the low turbidity within the channel.

SIT has recently received increased attention [21] owing to its potential use in all-optical switching applications [22], e.g., in optofluidic devices [23]. So far, SIT was predicted [24] and demonstrated in colloidal dispersions [22], where the driving force is the optical-contrast-dependent radiation pressure exerted on the colloids.

The precise mechanism of SIT in IS/ethyl acetate dispersions is not clear, especially the IS assemblies at the different stages. Nevertheless, a number of assertions can be mentioned. The observed irreversible SIT is
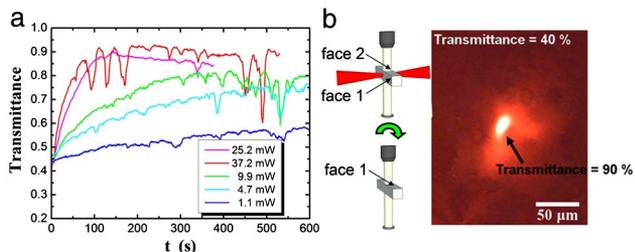
Fig. 3. (Color online) a, increase of the transmittance as a function of the irradiation time for different laser powers; b, transmission of the microscope's white light through the formed transparent microchannel (Tr = 90%). The background appears darker due to its lower transmittance (Tr = 40%). The image was recorded through white light illumination normal to face 1 of the cell. The sample is IS/ethyl acetate ($c = 0.038$ g/ml).

due to the local vanishing of the big aggregates that are either dissolved into smaller micelles or further aggregated into a polymer-rich solidlike skin formed around the tube, providing the observed stability. The final tube dimension and the conical front could result from the combination of self-defocusing and multiple scattering due to the large aggregates.

The proximity of phase changes in such dispersions [25,26] is also expected to play an important role worth studying. We could not at present establish whether the necessary mass transport needed for the observed SIT was purely diffusive or involved flow. Waveguiding was clearly observed, which suggested a specific refractive index profile formed during the process.

We believe the PI response to be at the origin of the unique SIT; to the best of our knowledge, such SIT is not present in other polymeric systems. The relatively short chains and micelles ($R_h < 20$ nm) are not expected to be responsive to optical forces at the utilized intensities (10^5–10^8 W/m^2). Similarly, light-induced thermal effects (thermophoresis or temperature-driven phase changes) are not expected [15] in the nonabsorbing dispersions. No thermal lensing was observed during the experiments with clear dispersions, hence confirming the absence of a strong thermal gradient.

In summary, we have explored the response to laser irradiation of PI-containing diblock copolymer dispersions. Whereas clear dispersions responded in a way similar to parent PI homopolymer solutions, turbid dispersions, due to the presence of metastable large aggregates, showed a unique case of SIT through the creation of broad transparent microchannels. Our understanding is that the light–PI coupling and the metastable turbidity are at the origin of the induced transparency. The rich phase diagrams of diblock copolymers in selective solvents offer an extra variable affecting the optical properties. Understanding the exact light–solvent–polymer interactions might uncover similar nonlinear effects in other complex fluids.

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