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Control of Chirality of an Azobenzene Liquid Crystalline Polymer with Circularly Polarized Light

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Abstract: Irradiation with circularly polarized light of a film of an achiral azobenzene liquid crystalline polymer induces chirality. Circularly polarized light with opposite handedness produces enantiomeric structures. A chirooptical switch based on this phenomenon is reported.

Introduction

Photomodulation of chiroptical properties of materials has stimulated considerable research interest that could lead to the development of materials for reversible optical storage. In solution, changes of the chiroptical properties (optical activity and circular dichroism) of polypeptides,[1] polyisocyanates,[2−6] polysaccharides,[7] and methacrylic polymers[8−12] containing a photochromic azo group and chiral groups could be induced by irradiation with unpolarized UV light. The geometric change induced by isomerization of trans to cis azobenzene produces in some cases conformational changes of the polymer backbone. A novel approach emerged recently, generating enantiomers with circularly polarized light (chiral) on photoresponsive materials. Switching a helical polymer between mirror images with circularly polarized light in dilute solution was demonstrated by Schuster and co-workers.[13] Switching of the screw sense of the helix in cholesteric liquid crystals by changing the chirality of a dopant with circularly polarized light was reported by Feringa et al.[14,15] and by Schuster et al.[16] In all these reports, the chirality is related to the presence of chiral side groups attached to the polymer backbone or to the addition of chiral dopants in liquid crystals.

In 1997 Nikolova et al. reported that very large circular anisotropy could be induced in films of liquid crystalline side chain azobenzene polyesters by illumination with circularly polarized light.[17] In this case, no chiral dopant was required. So far, these are the only reports where the circular anisotropy is induced in a polymer film using circularly polarized light as the only source of chirality. They initially proposed that a transfer of angular momentum from the circularly polarized light to the azobenzene chromophore leads to a new ordering after irradiation, thereby inducing chirality of the whole structure. They also concluded from their experiments that the induced chirality is the same as that of the light polarization, in keeping with the proposed mechanism.[18,19]

It is well-known that linear birefringence photoinduced in films of amorphous azobenzene polymers can be erased by irradiation with circularly polarized (CP) light. The explanation is that CP light activates the photoisomerization of all azobenzene groups in the plane of the film, restoring the preferred random arrangement of the chromophores.[20] We show here that in the case of a new liquid crystalline azobenzene polymer of a very similar structure to the most used amorphous polymer (**p4MAN**, Figure 1a), irradiation with circularly polarized light produces not a "random" state but a chiral, probably helical, arrangement.

Nikolova and co-workers observed the phenomenon by dynamic circular dichroism and optical rotation measurements at one wavelength (488 or 633 nm) while irradiating the sample with CP light. We use a complementary experimental approach, circular dichroism spectroscopy in the UV−vis region, after irradiation of the polymer film. In this case, CD bands are observed and their assignment allow identification of the functional groups involved in the chiral supramolecular structure. We also report the first optical switch based on the change of chirality in a prochiral polymer film using circularly polarized light as the unique source of asymmetric induction.

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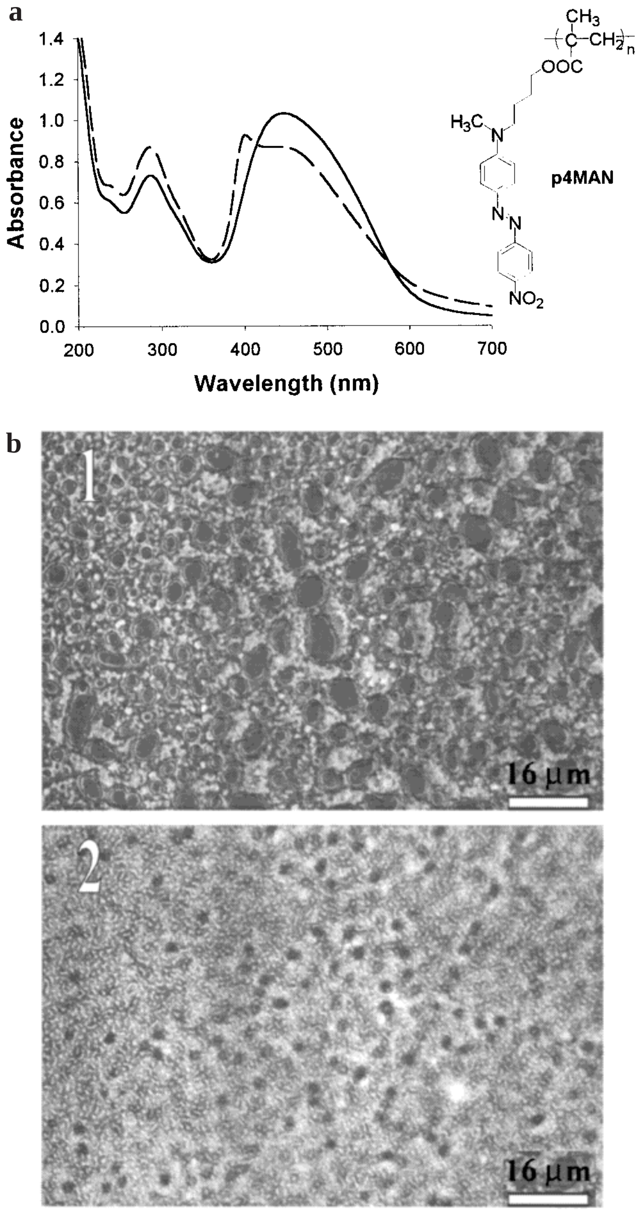
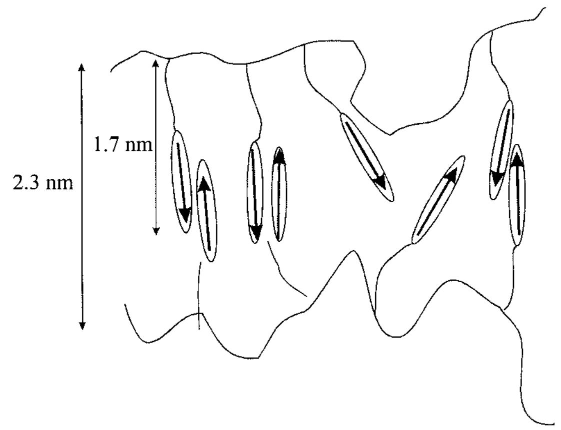


Figure 1. (a) Absorption spectra of **p4MAN** annealed thin film (140 nm) (smectic) before (- - -) and after (—) irradiation with CP light. (b) Optical microscopy images of a smectic thin film (1 μm) before irradiation (1) and after irradiation with a circularly polarized light (2).

Results

The detailed synthesis of **p4MAN** is described elsewhere.[21] The sample used was an oligomer with a glass transition temperature (T_g) of 74 °C. Above T_g, **p4MAN** films exhibit a smectic A phase, as identified by polarized microscopy and by X-ray diffraction patterns. The smectic layer spacing calculated from the X-ray diffraction is 23.4 Å, which is significantly larger than the calculated dimension of the side chain length, including the methylene spacer (17.1 Å). This, in combination with the UV–vis spectra,[22] suggests an antiparallel arrangement of the azobenzene groups with spacer and some of the backbone being part of the smectic layer as shown in Scheme 1. The film starts decomposing at 210 °C, before undergoing a smectic–isotropic transition.

Scheme 1



Two identical films of 140-nm thickness were prepared by spin-coating a solution of **p4MAN** in THF on fused quartz slides. After deposition, the films are isotropic, as verified by polarization microscopy. Annealing the films at 135 °C yielded a polydomain liquid crystalline (smectic-A) phase that is conserved after cooling to room temperature. The electronic spectrum (Figure 1a) shows a complex absorption band that can be ascribed to the presence of isolated chromophores ($\lambda = 446$ nm) and to the formation of smectic layers with interdigitated chromophores ($\lambda = 402$ nm).

The chromophores are initially isolated in the polymer after film preparation, but annealing can lead to an antiparallel interdigitation of the azobenzene moieties and the absorption band in the visible shifts toward shorter wavelengths.[23] **P4MAN** can thus produce an amorphous film and a smectic film, when the amorphous one is heated above T_g. For donor–acceptor substituted azobenzene groups, an antiparallel interdigitation of the chromophores arranged in pairs will tend to decrease the charge transfer between the electron donor group (amino) and the withdrawing group (nitro). Subsequently, the electronic transition will have a stronger $\pi-\pi^*$ than a $n-\pi^*$ character and a blue shift is observed ($\lambda_{max} = 402$ nm). The presence of the 446-nm absorption in the smectic film reveals that some of the chromophores are still isolated and are not involved in the smectic mesophase.[22]

Two films were heated to 135 °C to generate the smectic phase, then cooled to room temperature and irradiated for 15 min with circularly polarized light right (CP-r) and left (CP-l), respectively, with an argon laser ($\lambda = 514$ nm, $I = 75$ mW/cm^2). Irradiation in resonant conditions with a circularly polarized actinic light destroys the smectic layers by forming cis isomers. These metastable species will relax back to the trans isomers with a more random orientation, leading to a new state where more azo moieties are isolated and form smaller domains. The absorption band of this new organization is centered at $\lambda_{max} = 452$ nm (bathochromic shift) and still has a slightly asymmetric shape, which indicates some kind of organization in the irradiated area (Figure 1a). Also, as seen in Figure 1b, the film texture becomes smoother after irradiation and the holes (black areas) observed in the smectic phase almost disappear. Observations between crossed polarizers still indicate weak birefringent domains in the irradiated area, but atomic force microscopy measurements show that the size of the domains has significantly decreased.

The disappearance of the holes in the smectic phase can also be the result of a diffusion of whole polymer chains during

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irradiation. Such diffusion mechanisms have been reported for azo polymer materials as an explanation of the large periodic surface deformation.[24] This may be due to a bulk deformation of the polymer in the viscoelastic state and to a volume change during the photoisomerization process, with the cis isomer requiring a slightly larger volume, producing an internal pressure above the yield point of the polymer.[25]

By irradiation with CP light, the initially achiral films (no chiral center exists in the polymer) become chiral as observed by circular dichroism (CD) spectroscopy. The CD spectra are virtually complete mirror images of each other. Opposite CP light produced enantiomeric supramolecular structures.

The asymmetric pair of CD bands with a crossover point at about 290 nm can be assigned to a superposition of a split CD Cotton effect due to a high-energy $\pi \rightarrow \pi^*$ electronic transition of the azobenzene (in correlation with the UV−vis spectrum) with the CD band of the ester group from the methacrylate. The UV absorption of the ester group in **p4MAN** is at about 245 nm and is in agreement with the higher intensity of the left sideband when compared to the right side. Helical optically active poly-trityl methacrylate (poly-TrMA) showed a CD band at 232 nm, due to the electronic absorption of the ester groups of the methacrylate, regularly arranged along a helical main chain.[26,27] In **p4MAN** film, this band is red shifted by about 20 nm. This suggests a helical conformation of the polymer backbone after irradiation with CP light.

A second pair of CD bands of opposite sign with a crossover point around 425 nm is observed in the region of the azobenzene. It can be assigned to a split CD Cotton effect ($\pi \rightarrow \pi^*$ electronic transition) caused by electronic interactions between neighboring azobenzenes. This is generally associated with the existence of an ordered supramolecular arrangement with a prevailing handedness[10] (a helical conformation is suggested, based on the observed CD band of the methacrylate backbone). A split CD Cotton effect for the $\pi \rightarrow \pi^*$ transition of the azobenzene was, for example, observed previously in helical copolyisocyanates containing azobenzene side chain groups.[4]

When the film was irradiated with CP-l, a split CD Cotton effect which alternates from negative to positive signs going toward shorter wavelengths is obtained for the azobenzene electronic transitions. According to the chiral exciton coupling rules,[28] this indicates a left-handed screw sense of two coupled neighboring chromophores. We conclude that irradiation with CP-l produced a left-handed helical supramolecular arrangement of the smectic domains. CP-r produced a right-handed helical arrangement.

The ellipticity value of the right side CD band of this exciton couplet is about 1.5 times higher than the left side one (at about 400 nm). The asymmetry of this couplet can be tentatively assigned to the superposition of two CD effects given by two types of azobenzene chormophores that are in different chiral environments. The first one is a pair of CD bands of opposite sign (split CD effect, as discussed above) generated by coupled azobenzenes arranged in a helical manner. The second CD effect is a CD band given by isolated azobenzene groups disposed along parts of the macromolecule with a low degree of stereoregularity. A similar interpretation was previously used to explain the CD spectra of solutions of chiral azobenzene polymers with low degrees of stereoregularity.[10] Indeed, azobenzene polymethacrylates obtained by free radical polymerization are characterized by a low stereoregularity degree. They were shown to be syndiotactic in a proportion of up to 60%.[11] Thus, the probability of forming full helical main chain arrangements is relatively low.

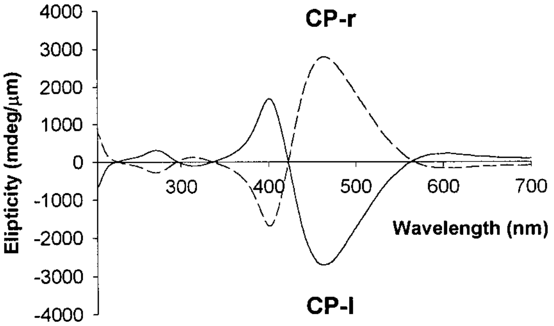

Figure 2. CD spectra of thin films (140 nm) of **p4MAN** recorded after irradiation with circularly polarized light (514 nm, 75 mW/cm^2): induced with CP-l (—) and with CP-r (- - -), respectively.

Further confirmation of the induced chirality was obtained by optical rotation measurements. Two annealed films (1.2 μm thick) were irradiated for 30 min with CP-r and CP-l, respectively, with an argon laser ($\lambda = 514$ nm, $I = 90$ mW/cm^2). The measured values for the optical rotation (546 nm) were very close (−2.40° for the spot irradiated with CP-l, and +2.28° for the spot irradiated with CP-r, respectively) and of opposite signs, as expected for enantiomeric supramolecular structures. This translates into an optical rotation of 20000 deg/cm.

Probably the most important result of this investigation is the possibility of switching between the two enantiomeric supramolecular structures by alternating irradiation with left and right CP light using a wavelength of 488 nm from an argon laser. In situ evolution in time of the induced circular dichroism is recorded at an operating wavelength (CP probe) of 488 nm. In Figure 3a,b, several cycles of induced chirality are presented. When the initial irradiation is done with a CP-r pump, the circular dichroism (at 488 nm, due to the azobenzene group) is positive, i.e. $A_{\mathrm{left}} > A_{\mathrm{right}}$, and reaches a plateau in about 60 s. After the pump is turned off, a weak relaxation is observed (less than 10% loss). Switching the pump to CP-l leads to a fast erasure of the CD, then a negative value of circular dichroism is produced. The initial dichroism is erased after 4 s of irradiation and 90% of the new opposite CD plateau is reached within 50 s. After a few cycles, the level of induced CD tends to decrease, indicating that the material exhibits some fatigue, as shown in Figure 3b. The fatigue is probably due to the orientation of some of the azobenzene chromophores perpendicular to the film plane. After photoisomerization, the cis azobenzenes are relaxing back to their trans form, which undergoes angular reorientation in the film plane, but also out of the film plane, so that finally the number of chromophores in the film plane tends to decrease. This may also induce a less favorable ability to re-form smectic domains.

To our best knowledge, this is the first example of a reversible chiroptical switching between two enantiomeric suprastructures, where the chirality is induced only by irradiation with CP light. Unlike previously reported chiroptical switches, the chirality is produced and switched exclusively by modulation of the circularly polarized light (left or right) and without addition of any chiral dopant in the prochiral polymer film.

No circular anisotropy could be induced in the amorphous film (not annealed), pointing out the essential role of the liquid

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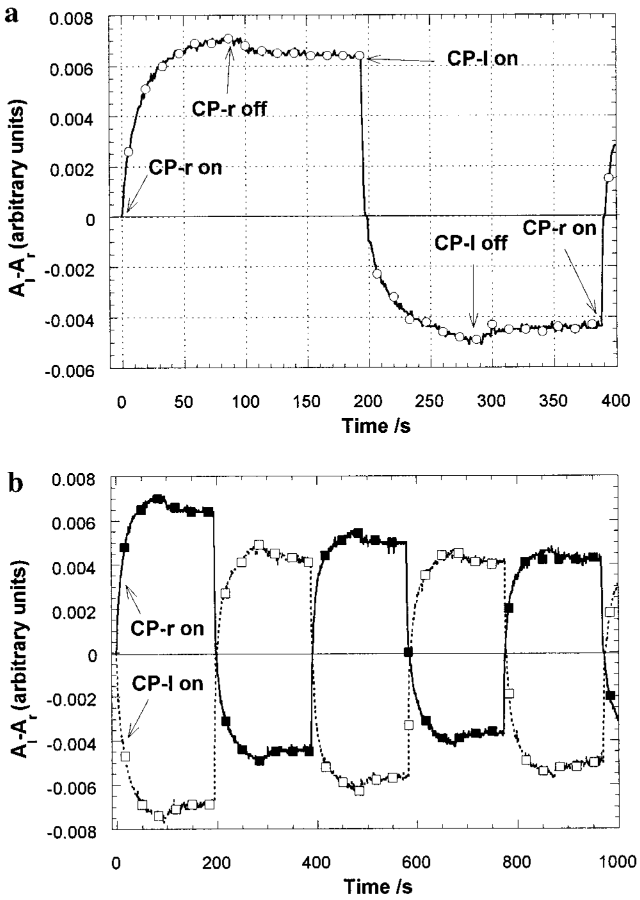


Figure 3. (a) Cycle of chirality switching. At $t = 0$ the film is irradiated with CP-r during 100 s followed by a relaxation (pump off) during the same period. At $t = 200$ s the pump beam is set to CP-l for 100 s. (b) Several cycles of chirality switching started initially with CP-r polarized light (full squares) or CP-l polarized light (empty squares).

crystalline arrangement. This also indicates that orientational preorganization is necessary.[18]

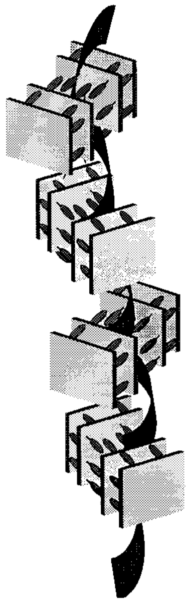
The photoinduced chirality is stable in time. An irradiated sample prepared as described previously did not show any decrease of the induced CD after a month. However, the induced circular anisotropy can be erased, either optically, by changing the sense of the circularly polarized light, or by heating the irradiated sample at 135 °C.

Discussion

A homeotropic (perpendicular to the substrate surface) arrangement of the azobenzene molecules, as initially suggested by Nikolova et al.,[19] is not probable in our polymer, since by irradiation the absorbance of the azobenzene increases (Figure 1a). The new model proposed by them appears to describe the phenomenon better.[29]

The source of the induced chirality is not fully understood, but a possible explanation can be given. Let us first consider that the film thickness can be divided in layers. When the circularly polarized beam impinges the first layer of the thin film no birefringence can be induced since the trans−cis isomerization followed by angular reorientation of the azo entities has the same probability in all directions. However, the small smectic domains of the first layer each have their own director that will change the polarization of the initial CP light to an elliptical state and at the same time they will undergo photoisomerization and angular reorientation. The sense of the induced ellipticity of the beam will be the same whatever the orientation of the directors of the various domains. The second layer will see a beam with an elliptical polarization that will induce the creation of a new optical axis within a new domain since the angular reorientation of the azobenzene molecules is polarization dependent; the polymer backbone can also move because it is linked to the photoactive azobenzene group. This stepwise approach can be extended along the successive layers of the film, but the change of ellipticity may not be linear along the film thickness since it depends primarily on the orientation of the director of each domain. Also, as the pump beam is absorbed by the film, its intensity decreases exponentially along the thickness. The key point is that the ellipticity, and therefore the orientation, of the optical axis of each domain is rotating in the same sense as the sense of the initial circularly polarized light, creating a chiral structure with the same handedness as the CP light. If the light is circularly left polarized, for example, the ellipticity of the light will vary with a left sense and the orientation of the directors of the new smaller domains will rotate gradually in the left direction along the thickness of the film so that the chiral structure has a left-handed helical conformation. Thus, the helical structure consists of grain boundaries where the directors are in the plane of the film and parallel to each other but are rotated in adjacent grain boundaries.

Scheme 2



The supramolecular structure generated by irradiation with CP light may be similar to a planar twist-grain-boundary (TGB) phase even if TGB or Sm-A* phases have been reported so far only when chiral mesogens are present.[30,31] A possible representation can be found in Scheme 2, where the polymer backbones exist mainly in the planes defining the smectic layers, but can also go between the various smectic grains, thus illustrating the potential for chirality of the main chain. The helix direction is along the film thickness (and the light propagation direction), and the azobenzene groups are mainly parallel to the film plane.

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The handedness of this helical structure is dictated by the handedness of the CP light. CP-l light induces a left-handed helical supramolecular structure and CP-r generates a right-handed helix. From all data in the literature, the existence of a pre-organized arrangement (smectic phase, and others) is essential to produce this supramolecular photoinduced chirality. At this stage it is less clear if nonpolar azo groups are capable of the same. Polarity favors interdigitation and antiparallel association, thus it may play a significant role in pre-organization. A variety of other azo polymers are being tested in our laboratory to verify this hypothesis.

Further information regarding the molecular arrangement in the film after irradiation by X-ray diffraction, pitch of the possible helix, and polarized optical microscopy (texture analysis) could not be obtained so far, because they require thicker film samples. In thick films the incoming beam is completely absorbed by the polymer film and the behavior could be different when compared to thin films.

Conclusions

We propose the formation of a TGB-like phase by the irradiation with CP light as a tentative explanation for the induction of chirality in an initially achiral Sm-A liquid crystalline azobenzene polymer. The existence of a photoinduced helical structure could not be proven by liquid crystal measurement techniques due to the thickness requirements for the film, but is suggested by circular dichroism measurements. We have proven the involvement of the azobenzene group, of the polymer backbone, and of the liquid crystalline arrangement as key factors for creation of the chiral suprastructure by irradiation with circularly polarized light. We are looking into the possibility of vibrational circular dichroism measurements in infrared spectroscopy which should provide additional information of the molecular ordering of each vibrational mode, separating the ordering of the polymer main chain and the ordering of the side chain chromophores. We are also investigating the role of other factors such as the type of liquid crystal, the interlayer thickness, and the type of azobenzene.

More importantly we report for the first time a reversible chiroptical switch between two chiral supramolecular structures in polymer films, where the chirality is induced only by the handedness of the light. This opens the possibility of utilization of such polymers for chiroptical switching.

Experimental Section

p4MAN (MW = 4700; polydispersity = 1.6) was obtained by free radical polymerization of the corresponding monomer in THF, using AIBN as initiator.[21] The average molecular weight and polydispersity of the polymer were estimated by gel permeation chromatography (polystyrene standard calibration), in THF, on a Waters liquid chromatograph equipped with a R410 differential refractometer. Films were prepared by spin coating solutions of polymers in THF onto clean glass and fused quartz microscope slides, and their thickness was determined with a Dektak profilometer. UV−vis spectra of films of polymers were measured on a Shimadzu spectrophotometer. Optical activity were measured with a Perkin-Elmer 241 Polarimeter (546 nm). Circular dichroism was measured with a Jasco J-715 spectropolarimeter. In situ dynamical measurements of induced circular dichroism have been performed at an operating wavelength (pump and probe) of 488 nm on thin films in their smectic phase (see Figure 4). The pump beam (75 mW/cm^2) can be polarized circularly left or right using a Babinet-Soleil compensator. The probe beam ($I = 0.02$ mW/cm^2) is modulated between left and right circular polarization at high frequency ($f = 50$ kHz) by a photoelastic modulator (Hinds, PEM 90). After signal conditioning,[32] the absorption differential signal is proportional to the circular dichroism (CD = $A_{\text{left}} - A_{\text{right}}$) and can be determined with an error of less than 1%.

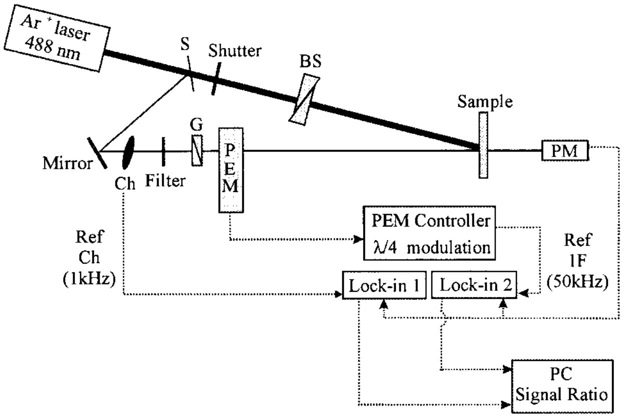

Figure 4. Experimental setup for dynamical recording of chirality switching: S, beam splitter; BS, Babinet-Soleil compensator; PM, photomultiplier; G, Glan-Taylor polarizer; Ch, chopper; PEM, photoelastic modulator.

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