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# Polarization of Soft Materials through Magnetic Alignment of Polymeric Organogels under Low Field Conditions

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**ABSTRACT:** Through application of an external magnetic field upon jellification of PHBV polymer in different solvents, an anisotropic organogel is obtained. This material presents two alignment steps in an external magnetic field, in the liquid phase and during the jellification, both phenomena measured by magnetic field induced linear birefringence. Remarkably, the organogel developed in this study presents a strong level of birefringence, 80 % of its maximum, in an external magnetic field as low as 2 T resulting from the magnetic alignment of the fibres of the material. This anisotropic material shows changes of absorbance upon rotation of a polarizer switching from “transparent” to “opaque”. In addition, its suprastructure does not influence the luminescent properties of encapsulated chromophores, allowing the formation of coloured anisotropic materials.

## INTRODUCTION

Since its introduction in the Nobel Prize lecture of Pierre-Gilles de Gennes, soft matter has been a new subject of science tackled by numerous research groups in the world.[1] This domain encompasses different classes of materials, such as liquid crystals, gels or elastomers, in which the molecular or macromolecular organic components are organized through self-assembly into soft materials defined by the mobility of some of their components, as opposed to crystals that exhibit long-range order of their constituents.[2] An exceptional feature of soft materials is their high responsive character to external stimuli that, accompanied by a change of the structural organization, leads to the formation of tailored soft matter[3, 4] with a large variety of applications, such as soft actuators,[5-7] artificial muscles,[8, 9] drug release devices,[10, 11] vibration absorbers[12] and switchable privacy windows[13] among others.

Although the self-assembly approach based on the supramolecular toolbox of non-covalent interactions (*i.e.* van der Waals forces, π-π stacking, H-bonding, electrostatic interactions or solvophobic effects) can lead to the formation of nanostructured materials exhibiting tailored functional properties,[14-16] top-down approaches usually are better suited to allow organization at higher scales (Figure 1). In this respect, the use of mechanical strength[17-21] or electric fields[22-28] can be considered alternative approaches to master soft-matter at the molecular organization level. Among all stimuli, the use of an external magnetic field appears promising, as it is non-invasive and contact-free, while being homogeneous over a large area. This leads to the alignment of macroscopic samples in a uniform manner.[29] This approach also presents the advantage to allow the preparation of anisotropic thin films as well as bulk materials. For instance, magnetic fields were reported to align soft materials such as liquid crystals,[30-36] carbon nanotubes,[37-44] molecular aggregates,[45, 46] peptide nanofibres,[47] steroid fibres,[48] colloidal nanocrystals,[49] polymers[50-52] or biological systems.[53]

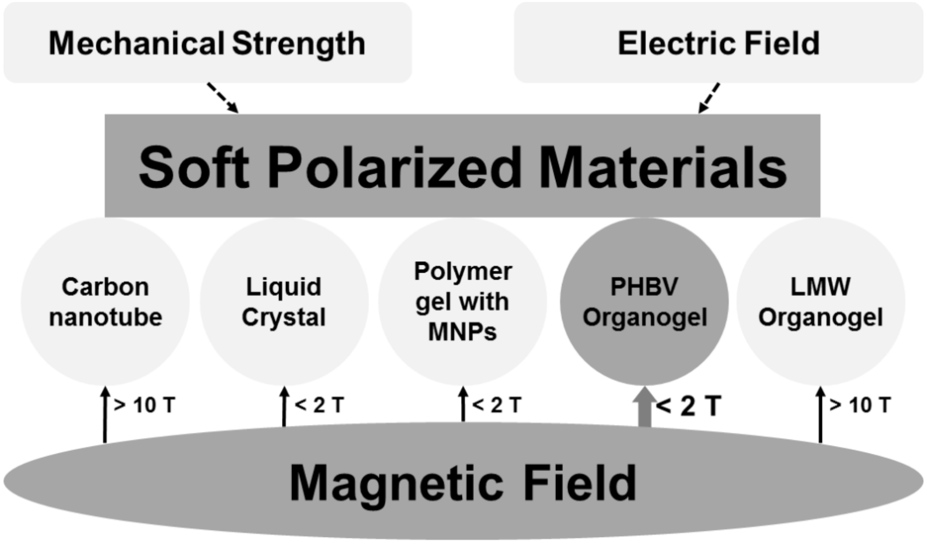

**Figure 1.** External stimuli used for the preparation of organized soft materials.

Among all examples of magnetically-organized organic materials, the manipulation of gel-based materials has emerged as a versatile route to prepare functional matter.[54-58] Along this line, Ishikawa and co-workers thus reported that the presence of an external magnetic field during the jellification of an agarose/methyl cellulose hydrogel leads to a change in their melting temperature.[59, 60] Recently, Aida and co-workers reported the formation of an anisotropic hydrogel composed, among other constituents, of metal-oxide nanosheets of titanate and niobate that aligns in the presence of an external magnetic field.[61] In this example, the alignment is triggered by the response of the metal-oxide nanosheets to the magnetic field. In a similar fashion, the development of magnetically responsive polymer gel has been studied.[62] These materials are prepared by the cross-linking of polymer networks and magnetic nanoparticles,[63, 64] the latter being the responsive constituents towards low magnetic fields. It is noteworthy to indicate that in very rare cases, polymer hydrogels without any addition of ferro-magnetic compounds were also reported in the literature.[65, 66] However, the alignment of organogels without the presence of magnetically responsive constituents is still very rare. To the best of our knowledge, the only example of stable organogel reported to date is described by Christianen and co-workers, who reported the magnetic alignment of a low molecular weight (LMW) organogelator constituted by an anthracenyl core.[29] However, compared to the magnetically responsive polymer gels described above, this material requires high magnetic fields (> 10 T) to undergo non-negligible alignment.

In this manuscript, we thus describe the alignment of a polymer-based organogel aligning under low external magnetic field (less than 2 T) without the presence of magnetic nanoparticles. As indicated before, magnetically aligned gels are very scarce and in particular magnetically aligned organogels, the latter requiring high magnetic fields to undergo alignment. In this regard, the description of an organogel aligning at 2T is very special. The polymer chosen for this study is poly(3-hydroxybutyric acid-co-3-hydroxyvaleric) acid (PHBV) with a PHV content of 8 mol%, a bio-sourced, biodegradable, and biocompatible polymer that belongs to the family of polyhydroxylalkanoates which are microbial polymers.[67] Poly(3-hydroxybutyric) acid (PHB) and its copolymers are amongst the most important bio-massed polymers and present good heat-resistance (up to 170 °C) and rigidity.[68-70] Capitalizing on the concept for which PHBV polymers can form organogels in toluene,[71, 72] we performed top-down alignment experiments exposing the organogels to a magnetic field and investigated its effect by *in-situ* birefringence studies. The structure of the organogels in the presence, or not, of a magnetic field was also verified by scanning electron microscopy (SEM). The formation of anisotropic materials was confirmed by polarized “incident light” and UV-Vis spectroscopy analyses. Finally, the ability of this new organogel to encapsulate organic chromophores leading to coloured anisotropic materials was also investigated.

## EXPERIMENTAL SECTION

*Preparation of the organogels.*

Without prior notice, the PHBV organogels used in this manuscript were prepared as follows: 44 mg of PHBV polymer stripes were dissolved in 1 mL of toluene, heating of the solution to its boiling point until complete dissolution of the PHBV stripes, addition of 0.5 mL of $CHCl_3$ at high temperature, transfer of the warm solution in a quartz cuvette and insertion of the cuvette in the magnetic field.

*Magnets used for the alignments of the organogels.*

Two different magnets were used to realize these experiments: a 32 T magnet with a 50 mm bore and a power of 18 MW in which the magnetic field is vertical and a 2 T magnet in which the magnetic field is horizontal. An optical apparatus able to measure *in-situ* the linear birefringence of the solutions was adapted in each of the magnets.

## RESULTS AND DISCUSSION

### *Magnetic Alignment of the PHBV Organogel: a mechanistic study.*

Depending on the co-polymer content, concentration and solvent one can obtained PHBV organogels with different physical and chemical properties. In this work, PHBV organogels were obtained by dissolution of PHBV stripes (44 mg) in toluene (1.5 mL), heating to the boiling point of the solvent and slow cooling to room temperature. Upon cooling, the solution starts to undergo jellification instantly. The magnetic alignment investigations were realized by transferring the warm solution in a 5 mm path-length quartz cuvette placed into a magnetic field. The time-dependent birefringence response was measured upon application of the external magnetic field.[29, 73] The magnetic birefringence originates from the anisotropy in optical polarizability of aligned molecules and manifests itself as a difference in the refractive indices for the light polarized parallelly and perpendicularly, respectively, to the magnetic field. While the magnetic field was maintained at 15 T, an increase of the absolute value of birefringence was observed upon application of the field, with the birefringence signal preserved upon turning off the magnetic field (see Figure S1). However, in toluene, the jellification started immediately after the sample preparation, thus sometime before application of the external magnetic field. As a result, the birefringence signal along with the degree of magnetic alignment was rather low (blue curve in Figure S1). The isotropic phase likely derives from those portions of gels that are already present and thus not affected by the application of the magnetic field. To decrease the jellification speed, a new protocol was developed using a mixture of solvents (toluene and $CHCl_3$, Figure S1). Addition of $CHCl_3$ as co-solvent decreases the jellification speed, giving sufficient time to apply a magnetic field before the initiation of the jellification process. Since no organogel is obtained in pure $CHCl_3$, the optimal solvent ratio was found to be a 2:1 toluene:$CHCl_3$ (Figure S2). As a result, the solution remains in its liquid form for approximatively 30 min before the jellification process starts, giving enough time to place the sample in an external magnetic field. Finally, the magnetic response of the material under application of a magnetic field (21 °C, ramp from 0 to 15 T at 50 mT/s and constant magnetic field at 15 T for 3 hours) was monitored. Clearly, one can observe two steps: one at low magnetic field and a second at the start of jellification (Figure 2).

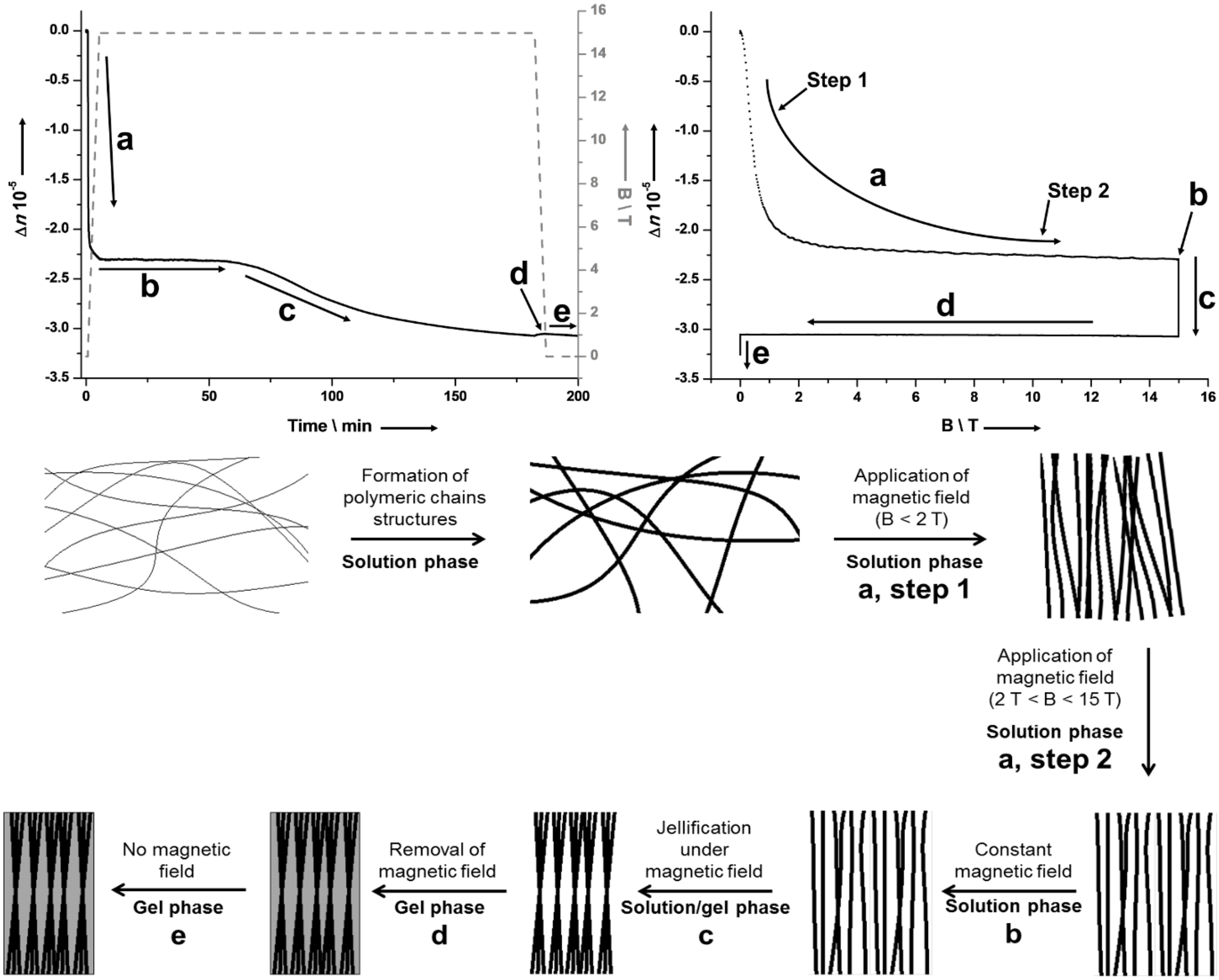

**Figure 2. Top:** Birefringence measurements during the jellification of PHBV polymer in a 2:1 mixture of toluene and $CHCl_3$ under the external magnetic field. The left panel displays the birefringence signal (solid line) and the change of the magnetic field (dashed line) as a function of time; whereas the right panel displays the same birefringence signal as a function of applied magnetic field. The jellification process proceeds through the steps a-e. *a*: change of birefringence of the sample in the solution phase upon increase of the magnetic field intensity (*Step 1*: B less than 1 T, *Step 2*: B between 1 to 15 T) that causes an alignment of the polymeric chains structures in the solution; *b*: plateau of birefringence in the solution phase upon constant magnetic field of 15 T that corresponds to a saturation of the polymer alignment under these conditions; *c*: change of birefringence during the jellification process that most likely corresponds to the formation of non-covalent fibres constituted by the single polymeric chains; *d*: conservation of the birefringence upon decrease of the magnetic field from 15 to 0 T; *e*: slight change of birefringence at 0 T upon the end of jellification. **Bottom:** Schematic representation of the proposed jellification steps under magnetic field. In a first venue, the polymer chains create larger structures (as can be seen in the SEM pictures presented thereafter) in the solution phase.

Five regions can be distinguished in the time- and magnetic-field dependent birefringence spectra. Upon application of the magnetic field, the material presents a steep change in the birefringence while still being in the liquid phase (Figure 2, Top, a, step 1). In the first step, with B lower than 2 T, the birefringence dramatically decreases suggesting a strong alignment of the polymeric chains structures in the solution phase under the external magnetic fields (Figure 2, Bottom, a). Upon dispersion of the polymer in toluene, ordered structures are spontaneously formed, as shown later in the SEM pictures, with a large enough magnetic anisotropy to undergo alignment under application of an external magnetic field (Figure 2, Bottom). It is noteworthy to indicate that upon increase of B from 2 to 15 T, the change of the birefringence response is gradual, indicating that the material is very responsive to magnetic fields and that most of the alignment occurs at low field (Figure 2, Top, a, step 2).

Upon maintaining the magnetic field at 15 T, the birefringence maintains a constant value (Figure 2, Top, b). This behaviour indicates that the alignment of the PHBV polymer has reached its maximum after a few minutes, suggesting a very fast polarization process in solution. As the jellification starts, another significant variation in the birefringence response can be clearly noticed (Figure 2, Top, c). This is attributed to a bundling process involving the single polymeric PHBV chains that trigger to the formation of the gel. Obviously, these new suprastructures will display a different response towards magnetic fields compared to the single polymer chains in solution (Figure 2, Bottom, c). Finally, upon removal of the magnetic field, the birefringence signal does not undergo significant changes (Figure 2, d) ultimately confirming that the gel retains its organization (Figure 2, e). Notably, the global anisotropy of the material keeps on increasing even after turning off the magnetic field (Figure 2, e). This behaviour is probably triggered by an induced dynamic organization between aligned and non-aligned fibres, for which the occurring of the alignment propagates well after the removal of the magnetic field.

These mechanistic hypotheses were confirmed by performing birefringence measurements of solutions containing PHBV under application of a magnetic field sweep from 0 to 15 T. Three different concentrations (using 29.3, 7 and 0.73 mg/mL of PHBV) were thus tested (Figure S3). As expected, these solutions did not undergo jellification during the time of the sweep experiments to 15 T (around 20 min), even if the solution with 7 mg/mL jellified at a later time. All solutions presented a similar behaviour and only the size of the birefringence signal scales linearly with the PHBV concentration, in accordance with birefringence theory.[74] These results indicate that the PHBV polymer presents structures of comparable size at low and high concentration and that both respond similarly to the magnetic field stimuli.

Screening different jellifying solvents led to similar conclusions. Namely, in pure DMF or $CHCl_3$, the response of PHBV in solution is very similar to that reported in toluene or in its mixture (Figure S1). Similarly, a change in the ratio $CHCl_3$/toluene does not influence the responsive behaviour of the solution upon a sweep of the magnetic field, as long as the jellification process does not start before the application of the magnetic stimulus (Figure S2). This also enlightens that the solvent medium is not a predominant factor in the alignment of the PHBV polymer in solution. It is noteworthy to indicate that acetone and EtOH were also used, but no valuable conclusions could be drawn due to the very low solubility of PHBV in these solvents even under reflux conditions.

*Influence of the Magnetic Field Intensity.*

In order to validate the hypotheses described above, we have studied the response of the PHBV polymer as a function of the external magnetic field intensity. These experiments were realized following the procedure previously described, namely through the application of a magnetic field with a ramp of 50 mT/s and maintaining of the field at a given intensity for three hours. As expected, an increase in the field intensity leads to a higher degree of polarization of the organogel (Figure 3, Top). While the response of a solution of PHBV is proportional to the magnetic field intensity up to 15 T, no noticeable differences were observed for higher values. This result indicates that the magnetic saturation of a solution of PHBV polymer happens for a magnetic field intensity of approximately 15 T (Figure S4).

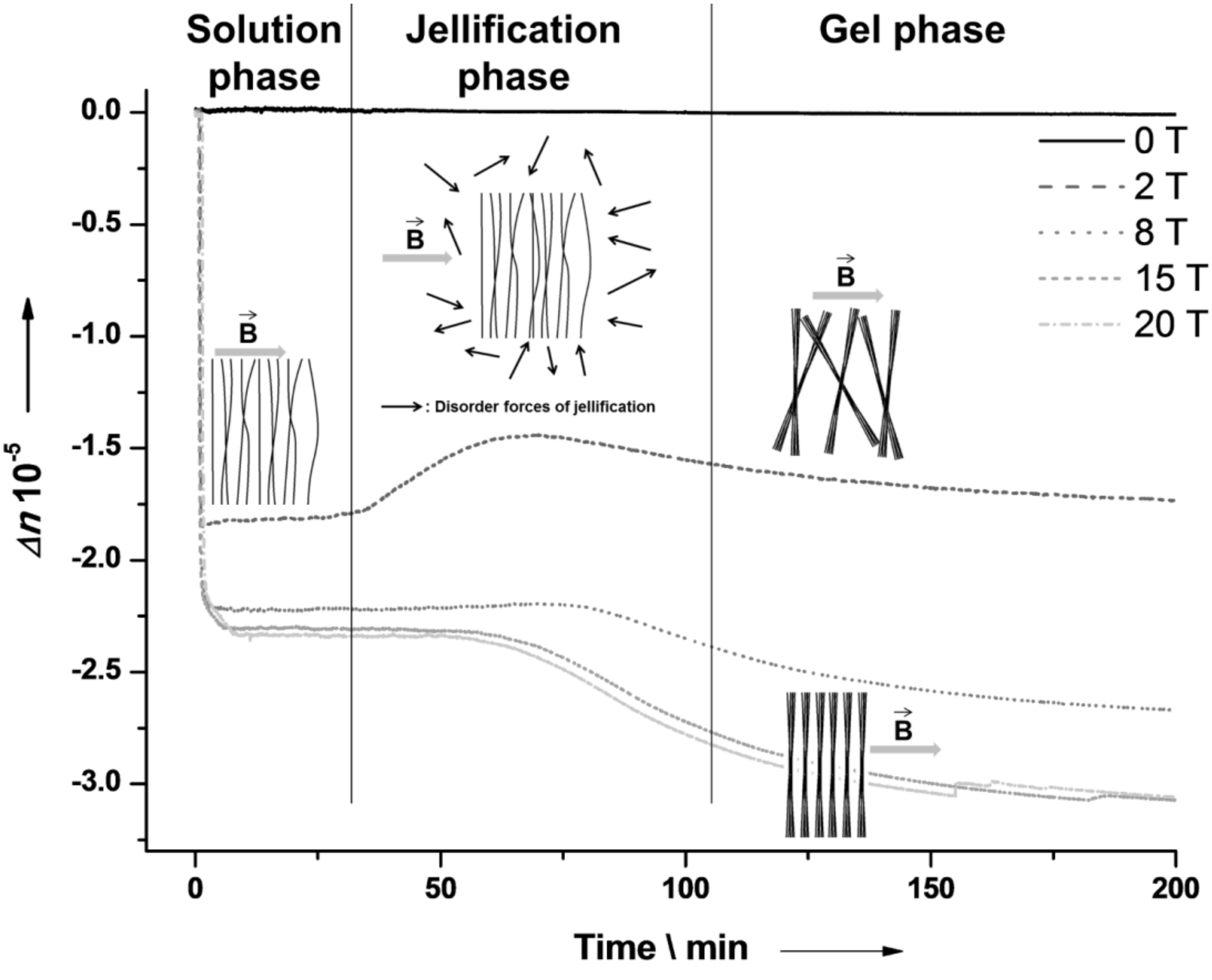

**Figure 3.** Birefringence response of the organogel as a function of the magnetic field intensity. No birefringence response (i.e., no alignment) is present in the absence of any magnetic field, whereas when a field is applied the optical property evolves in two steps, during sweeping up the field and during the jellification. In the scheme, entropy-driven disorder forces take place during the jellification process influencing structural polarization of the materials under the different magnetic fields. Their effect is suppressed when magnetic fields higher than 8 T are used.

On the other hand, a clear change of the birefringence response at the beginning of the jellification differs for different magnetic field strengths. While at 15 and 20 T the birefringence response of the sample suggests that the overall alignment of the sample increases, a different behaviour is observed at lower magnetic fields. Under a 2 T field, the macroscopic anisotropy of the material first decreases and after a while it increases. An attenuated, yet similar, trend showing a slight decrease of the birefringence value followed by an overall intensification was also observed for the samples exposed to 8 T field. At the mechanistic level, the loss of anisotropy during the jellification phase under magnetic field lower than 8 T field, is likely to be triggered by entropy-driven structural fluctuations that originates during the formation of the bundled structures (Figure 3, indicated as disorder jellification forces). The formation of bundle-like structures was confirmed through SEM analysis (see below) of the materials sampled at different times during the jellification process.

*Morphological Characterization through Scanning Electron Microscopy (SEM).*

To morphologically study the material organization upon jellification, SEM analyses of the Xerogels formed from a given solvent were performed. After introducing 10 mg of PHBV polymer and 1.5 mL of the desired solvent in a vial, the mixture was heated to reflux. A drop of warm solution was placed on a silicon wafer and the solvent was slowly evaporated at room temperature and atmospheric pressure. The sample was further dried under vacuum and the materials coated with 10.2 nm of Au. As one can see in Figure 4a and S5, the solution prepared from toluene show the formation of fibres, whereas undefined aggregates (Figure 4b and S6) were observed when prepared from a $CHCl_3$ solution. SEM pictures of the organogels show clear morphological differences between samples formed in the presence or in the absence of the external magnetic field. In the absence of a magnetic field, the organogel presents a porous 3D structure constituted by isotropic entwined fibres (Figure 4c and S7). The fibres present a twisted shape with a width between 300 and 550 nm and expand in all directions. It should be pointed out that the fibres have a strong similarity compared to those obtained with the toluene solution previously depicted in Figure 4a. On the other hand, when the organogel is prepared under the exposition of a 2 T external magnetic field, a homogenous orientation of the fibrous material is apparent (Figure 4d-e-f, S8 and S9). Contrary to the organogels prepared in the absence of a magnetic field, SEM images of the aligned xerogels show the presence of bundles of fibres that are mostly oriented perpendicularly to the applied magnetic field. The perpendicular magnetic orientation of the fibres was confirmed by the estimated theoretical molar magnetic susceptibility ($\chi$) of the polymer backbone (Figure 4g). In particular, considering that the diamagnetic susceptibility of an organic molecule is given by the sum of the contributions of each functional groups (see also the SI),[75] it is possible to estimate the theoretical magnetic susceptibility of a given molecule. Considering the monomeric unit of PHBV (Figure 4g), the molecular susceptibility in the y-direction is estimated to be the highest, thus determining the alignment direction. These experimental findings further validated our organization hypotheses, for which the bundles are formed upon jellification when the samples are exposed to an external magnetic field (Figure 2, Bottom).

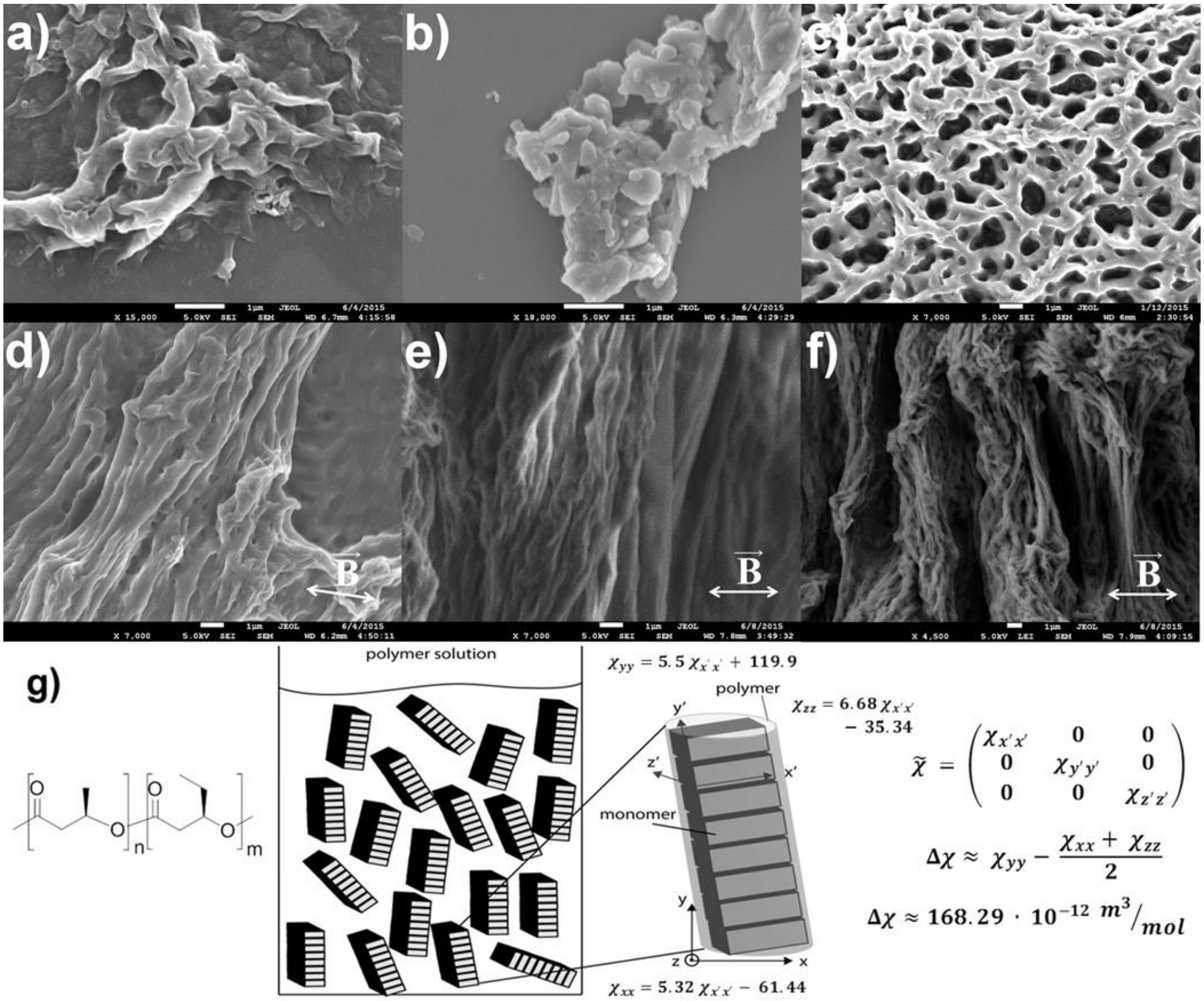

**Figure 4.** SEM pictures of solutions of PHBV in a) toluene and b) $CHCl_3$ and organogels in the c) absence or d,e,f) presence of 2 T field (in each picture the scale bar corresponds to 1 µm). g) Schematic representation of the polymers in solution. The polymers are treated as aggregates with the monomers as the molecules building the aggregates with cylinder symmetry. (x, y, z ) is the lab frame of axes and (x', y', z' ) is the frame of axis for the molecule (monomer).The estimated values of the molecular magnetic susceptibility (χ) of the monomer units constituting the polymer backbone (x', y' and z' are the principal molecular axes while and x, y, z are the lab axes) are shown.

*Study of the Anisotropic Organogel through Analyses with Polarized Light.*

The formation of an anisotropic organogel at the macroscopic level was verified by polarized “incident light”. This analysis was performed by measuring the optical response as a function of the “optical” angle $\theta$ (Figure 5a), defined as the angle between the direction of the magnetic field applied during jellification and the axis of the linear polarizer. Specifically, when $\theta$ = 0°, the anisotropic gel presents a minimum in light absorbance that leads to a “transparent” material, whereas at $\theta$ = 90° the spectrum shows a maximum in the absorbance rendering the material “opaque” (Figure 5b). As expected, organogels prepared in the absence of any magnetic field does not present any anisotropic optical behaviour. Complementary polarized UV-Visible absorption spectroscopy also confirmed the formation of anisotropic materials. Due to the overall absorbance of the material as well as the cost of the experiments, these tests were realized in 2 mm path-length cuvettes in a 2 T magnet. When the polarizer is rotated from $\theta$ = 0° to $\theta$ = 90°, the absorbance of the material significantly increases (Figures 5c and S10-12), further confirming the polar opacity observed for the materials shown in Figure 5. Reference measurements realized with non-magnetically-aligned organogels demonstrated no change in the absorbance upon rotation of the polarizer, ultimately confirming the macroscopic anisotropy of the material.

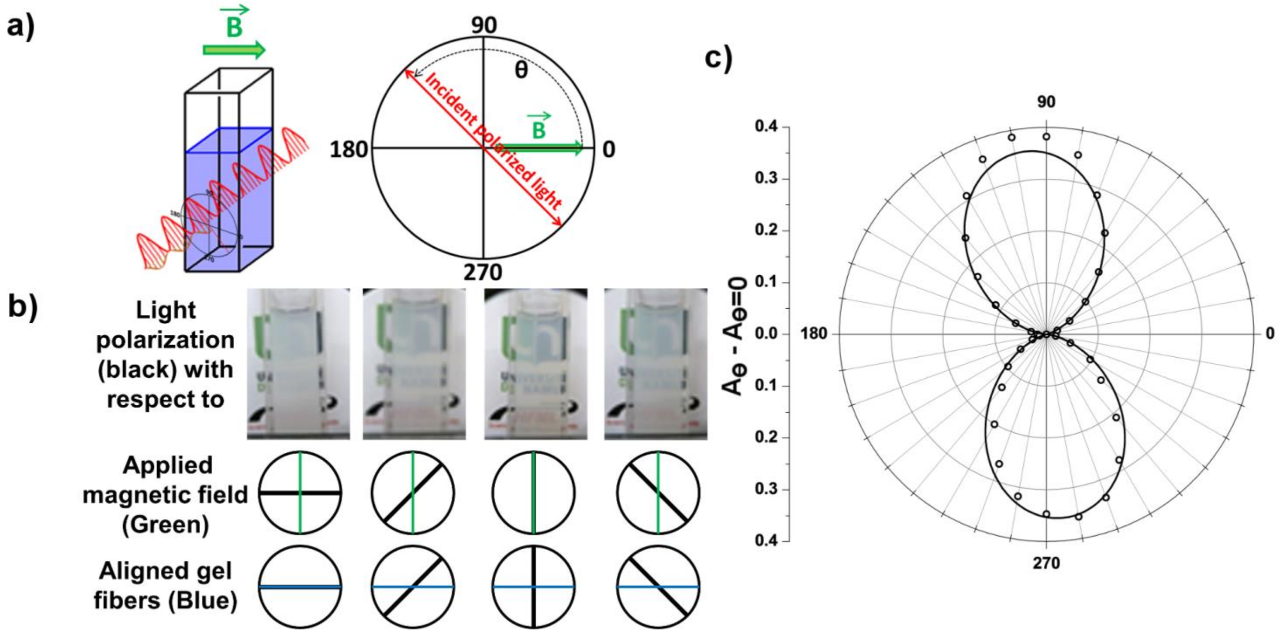

**Figure 5:** a) Schematic representation of the interaction between an anisotropic material and polarized light; b) photographs of the anisotropic organogel as a function of different "optical" $\theta$ angle (the black line corresponding to the direction of the applied magnetic field, while the green line corresponds to the plane of the polarizer and the blue line to the alignment direction of the gel fibres); c) polar graph of the organogel at 571.39 nm.

Formation of Coloured Anisotropic Organogels.

In addition to the formation of anisotropic material, we exploited the organogel as a matrix to encapsulate chromophores to prepare coloured materials that could change from "opaque" to "transparent" upon rotation of a polarizer. In this regard, three core-substituted naphthalene diimides synthetized in our laboratory were chosen for the preparation of coloured anisotropic organogels (Figure 6).[76-78] Each of these asymmetric naphthalene diimides possesses either ethoxy or isopropylamino moieties that lead to different optical gaps.[77] As a result, each of these molecules differs in colour, with the molecule bearing two ethoxy substituents appearing yellow, that with one ethoxy and one isopropylamino group being red and that with two isopropylamino moieties displaying a blue tint. In order to study the reciprocal influence on the photophysical properties of the material of both PHBV and chromophores (Chrs), the absorbance, emission and excitation spectra of each chromophore in solution and in the organogel (Chr@organogel) were recorded (Figure 7). The emission spectra of the chromophores in the solution and in the organogel matrix are very similar and reflect the fact that the polymers do not have any electronic influence on the luminescent properties of the embedded chromophores. It is noteworthy to indicate that while the absorbance spectra show differences between the samples in solution and in the gel, essentially deriving from polymer-centered electronic transitions, the excitation spectra are very similar. This indicates that no significant interactions are established between the polymer and the chromophores and only a strong scattering is observed. The comparable photophysical properties of the chromophores in solution to those of Chr@organogel suggest that one can tailor materials displaying programmed colour and fluorescence signals, the functionality of which is solely dictated by the constituting dyes.

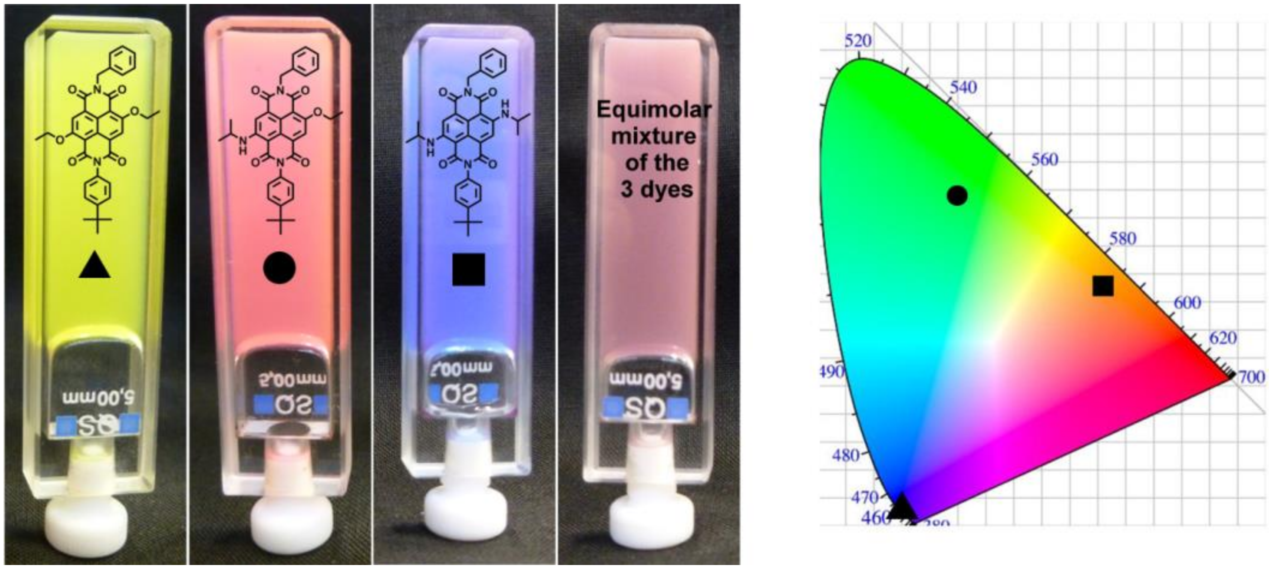

**Figure 6. Left:** Picture of the different organogels containing the three chromophores and an equimolar mixture of the three dyes. **Right:** Chromaticity diagram built from the absorbance spectra of the three chromophores.

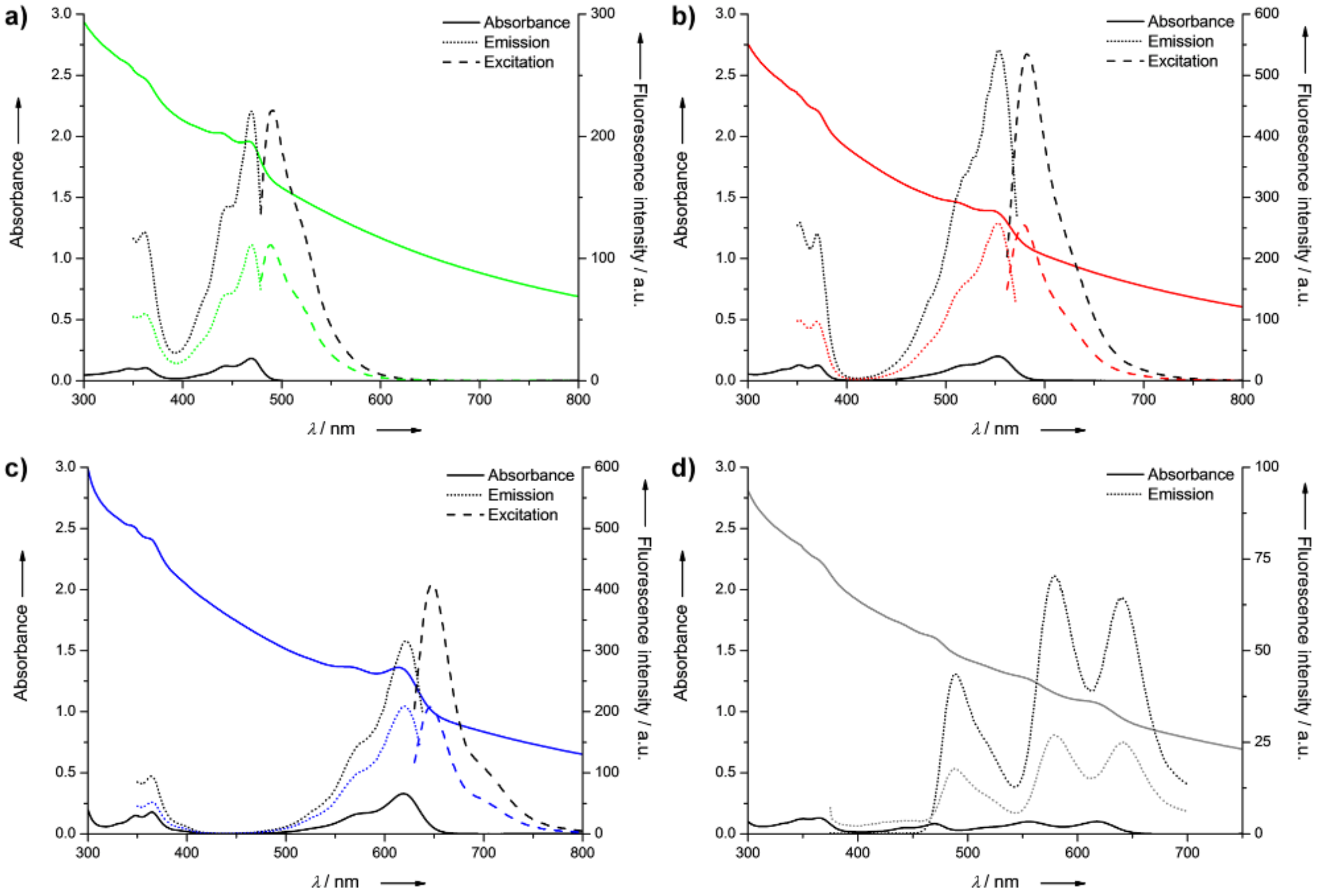

**Figure 7:** UV-Vis, emission and excitation spectra of the chromophores in solution (black lines) and in the organogel (coloured lines) for the **a)** yellow, **b)** red, **c)** blue and **d)** mixture of the three chromophores. The concentrations of the chromophores in the Chr@organogel hybrids were identical to those of the solutions.

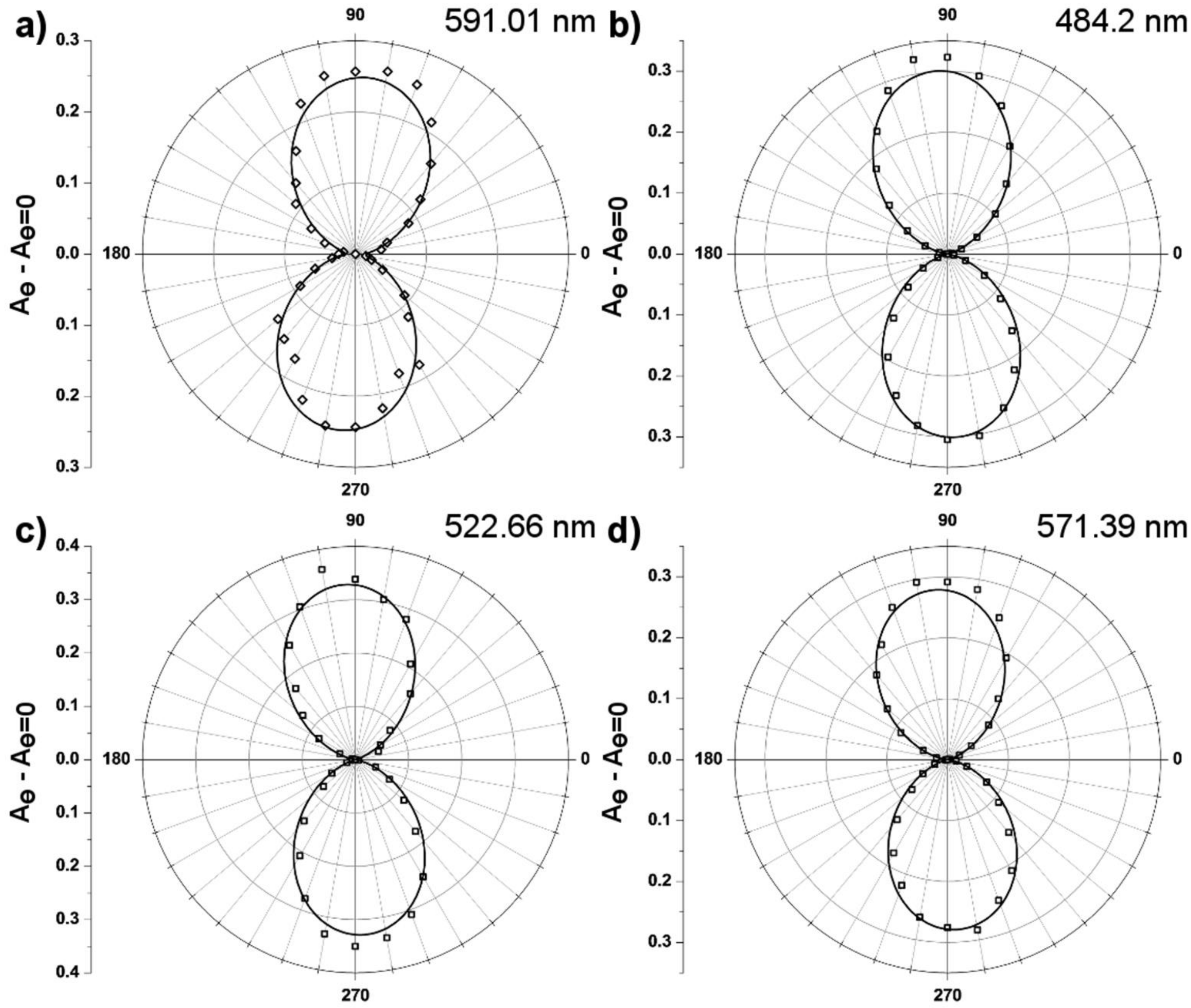

**Figure 8:** Difference of absorbance ($A_\theta$-$A_{\theta=0}$) as a function of the "optical" angle $\theta$ for the four Chr@organogel hybrids at given wavelengths (a: blue@PHBV, b: yellow@PHBV, c: red@PHBV, d: red-blue-yellow@PHBV).

The polarization of the coloured organogels was thus realized by applying an external magnetic field at 2 T. After jellification, the polarized "incident light" reveals a similar behaviour for the Chr@organogel samples as compared with the non-coloured organogel. The anisotropic properties of the coloured materials were verified by polarized UV-Vis spectroscopy that, revealing an absorbance change upon rotation of the polarizer, confirmed the visual switching from "transparent" to "opaque" when passing from optical angles $\theta = 0°$ to $\theta = 90°$ (Figure 8 and SI). It is noteworthy to indicate that even if the samples present anisotropic optical properties, the UV-Vis absorbance spectra reveal that the incorporation of the chromophores is not affected by the polymer alignment, thus suggesting that the chromophores are dissolved in the solvent domain as isotropic entities. This further supports the idea for which the sizes of the organogel pores (Figure 4c-f) are large enough to create localized domains confining isotropic solution phases. Given this property, the cavity-confined chromophores are not spatially constrained and keep their thermal motion after removal of the external magnetic field. As a result, the chromophores do not feature any preferential orientation in the final material while the anisotropy of the polymeric framework in the gel is preserved.

## CONCLUSION

In this paper, we have reported the preparation of an organogel from a biodegradable polymer that, under the exposition of an external magnetic field, can align giving rise to a very rare example of anisotropic organogel materials. Noticeably, the organogel can be aligned under low magnetic fields (as low as 2 T), which is unprecedented for this kind of materials. This presents the advantage of requiring low energy and simple inexpensive equipment. The organogel could be implemented in optical materials that can switch from “transparent” to “opaque” upon rotation of a polarizer. The encapsulation of molecular chromophores did not affect the alignment of the fibres while conserving their intrinsic luminescent properties. This allowed us to obtain anisotropic materials able to keep their colour while becoming “transparent”. Future directions are aimed at the development of new, white or coloured as required, privacy devices based on polarized light.

## ASSOCIATED CONTENT

**Supporting Information**. Magnetic susceptibility theoretical estimation, birefringence measurements, SEM pictures, polar graph and UV-Vis absorption spectra of white and coloured organogels.

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### Author Contributions

All authors have given approval to the final version of the manuscript.

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## ABBREVIATIONS

PHBV poly(3-hydroxybutyric acid-co-3-hydroxyvaleric) acid

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