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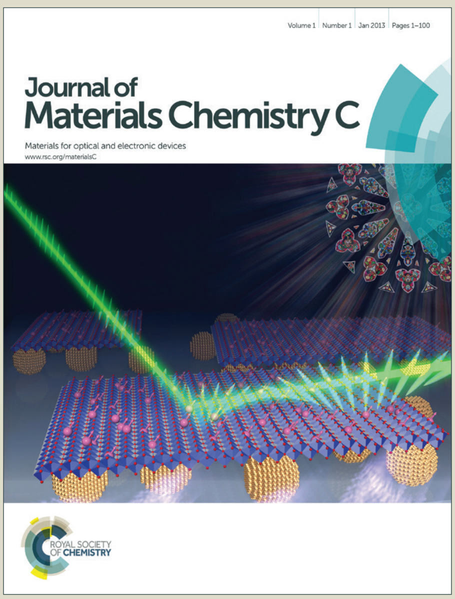

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ARTICLE

A New Twist on Cholesteric Films by using Reactive Mesogen Particles

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An innovative approach to producing reflective systems is presented by using Reactive Mesogen based Cholesteric Particles (ChRMPs). The versatility of the novel ChRMPs opens the door to produce single- or multi-wavelength reflective systems by mixing particles with Bragg reflection located at different wavelength values. Particulate based films can be prepared in absence of any alignment layer on any kind of substrate with very wide viewing angle behaviour, which is in clear contrast to conventional reflective films based on cholesteric liquid crystals with planar alignment. The straightforward film preparation, flexibility of the synthesis and the excellent viewing-angle property make ChRMPs a very interesting new approach to produce reflective films for applications including, but not limited to, flat panel display such as in brightness enhancement or colour filters.

Introduction

Chiral droplets have attracted much attention in recent years from a theoretical approach[1-4] and describing their optical manipulation or lasing performance.[5-9] The number of examples about solid chiral particles is very scarce. Recently, Ciparrone et al. reported the preparation of polydisperse solid particles exhibiting isotropic or a blend of different anisotropic modes of reflection.[10-12] However, there is not reported an insight into transferring this kind of particles generated in a colloidal system into film applications.

Cholesteric liquid crystals (ChLCs) exhibit a twisted director that is orthogonal to the long axis of the molecules. Due to this supramolecular arrangement, ChLCs have the ability to reflect 50% of the incident non-polarized light with a determinate wavelength as circularly polarized light with the same handedness as the helix. Meanwhile the other 50% of the light will be transmitted through the helicoidal supramolecular arrangement.[13-14] The central reflected wavelength value is related to the average refractive index of the material and the optical pitch ($\lambda o = Po\ n_{ave} \cos \Theta$) where Po is the pitch length (2π helical turns of the nematic director), n_{ave} is the average refractive index and $\cos \Theta$ is the viewing-angle from normal incidence. The latter term is responsible for the off-axis angle dependence of cholesteric films or flakes which shifts the reflection to shorter wavelength values.[15] It has been reported that colour shift can be reduced by coating reactive mesogens on hemi-spherical micron-patterned substrates.[16-17] Therefore, we focused our efforts in the applicability of ChRMPs with a radial director configuration in reflective films. Three very attractive advantages are expected for this kind of particle. Firstly, the use of an alignment layer or alignment additives is not required for aligning the cholesteric material on the substrate. Secondly, a very low viewing-angle dependent colour shift is expected for ChRMPs because the influence of $\cos \Theta$ in the reflected λ value will be suppressed as a consequence of spherical confinement of the helical axis in a radial configuration (Figure 1). Finally, all these optical properties are acquired directly from the synthesis, and a simple dispersion of the particles into a binder and subsequent coating on a suitable substrate is all that is required to produce a reflective film. Besides, each particle has a well-defined director orientation which is independent of the other particles and it might make feasible to produce multireflective systems by mixing particles reflecting different wavelengths values. Opening an alternative for producing broad-band cholesteric films without the need for a complicated curing procedures comprising diffusion effects, templates and / or UV gradients along the cholesteric films[18-23] under controlled oxygen atmospheres[24] or multilayer systems.[25]

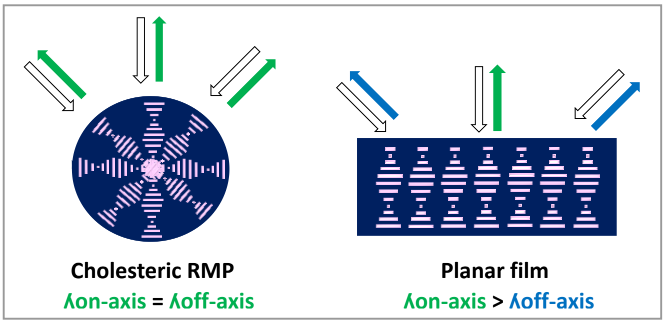

Fig. 1 ChRMPs *vs* cholesteric planar film optics illustration.

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Results and Discussion

Monomer Mixture and Phase Behaviour

Monomer mixture contains reactive mesogen RM257, RM520 and the chiral RM894 (Merck Chemicals), photoinitiator Irgacure®369 (BSAF) and photoinhibitor Irganox®1076 (BSAF) (see Supporting Information). In order to ensure a good blend of all components, monomer mixture is heated at 160°C for two minutes under stirring. After this time, the solution is cooled down to room temperature. The liquid crystal behaviour was studied by polarised optical microscopy (POM) and differential scanning calorimetry (DSC) (Figure S1 and Figure S2). Red, green and blue monomeric mixtures exhibited very similar phase behaviour and transition temperatures. On first cooling process from the isotropic state, an isotropic – cholesteric phase transition around 124°C is present. The mesophase remains metastable below room temperature under the given experimental conditions. On second heating, the transition cholesteric – isotropic liquid is observed around 128°C. Solvent responsive monomeric mixture exhibited an isotropic – cholesteric transition at 146°C when cooling from the isotropic state. On second heating, a cholesteric – isotropic liquid phase transitions takes place at 149°C.

Synthesis

ChRMPs (4.7±2 microns) were prepared by suspension polymerization (Figure S3). The main points considered when designing the synthesis were the ability to prepare particles with a controlled size, batch-to-batch reproducibility and, in principle, possibility of scaling-up the synthesis. Reaction conditions and formulation were optimized to obtaining particles with an average size below 10 microns. Once the formulation was optimised the size was controlled by the stirring power (Figure S4). In a first step, monomer mixture is heated at 90°C where the cholesteric phase is ensured. Once the temperature is stable, the mixture is kept at 90°C for 5 minutes and a preheated surfactant solution in dodecane at 100°C is added on the liquid crystal monomeric mixture. Immediately, the emulsion is formed by using an IKA homogeniser (T25 digital Ultra-Turrax®) for 20 minutes at 14600rpm. The previously formed emulsion is added to a flask previously heated at 90°C and the polymerisation is initiated under UV light irradiation for 15 minutes. Polymer particles formed are filtered by using a 50 micron filter cloth and are centrifuged at 10000rpm for 10 minutes. After the first centrifuge cycle, particles were washed with dodecane twice and toluene until the solution is clear. At this point, any side-product and surfactant has been removed from the solution and only particles in a clean solvent are present (Figure S5 and Figure S6). Optical thermal stability and optical solvent resistance were checked by heating the particles up to 220°C and transferring them into different solvents such as dodecane, heptane, ether, toluene or water (Figure S7). Even though good optical solvent resistance can be achieved, the versatility of the synthesis makes possible to prepare solvent responsive ChRMPs with a reversible change of the reflected light by lowering the cross-linker content. The inner part of the particles was analysed by cross-section TEM analysis. The images revealed an onion-like structure which proposes the helices originating from the center to the edges (Figure S8).

Cholesteric Reactive Mesogen Particles based Dispersions

Cholesteric droplets and ChRMPs were observed by polarised optical microscopy in transmission and reflection mode. During the synthesis process, monomer droplets are initially formed in the emulsions. The selective Bragg reflection only occurs in these unpolymerised droplets and not in the continuous phase. Once polymerization has taken place, the Bragg reflection also occurs in the cholesteric particle (Figure 2 and Figure 3).

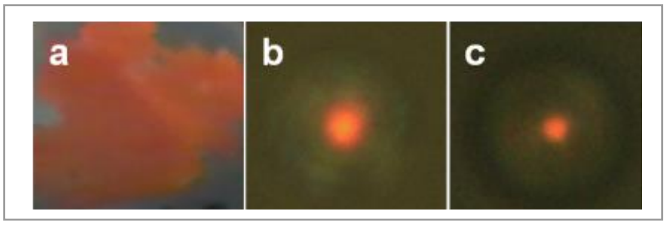

Fig. 2 (a) Red cholesteric mixture, b) Red cholesteric droplet and c) Red ChRMP.

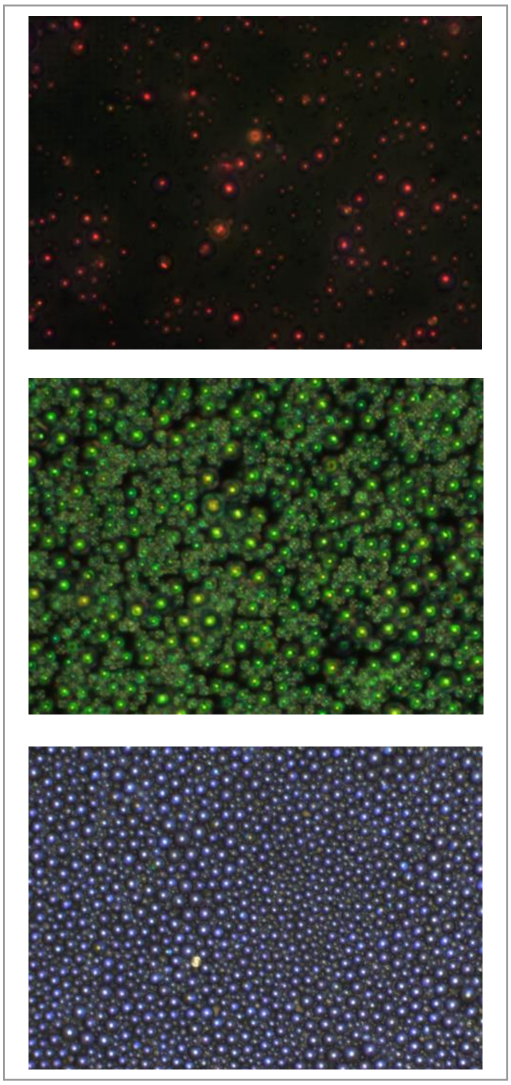

Fig. 3 Polarised optical microscopy images corresponding to red, green and blue dispersion in quinoline (x20).

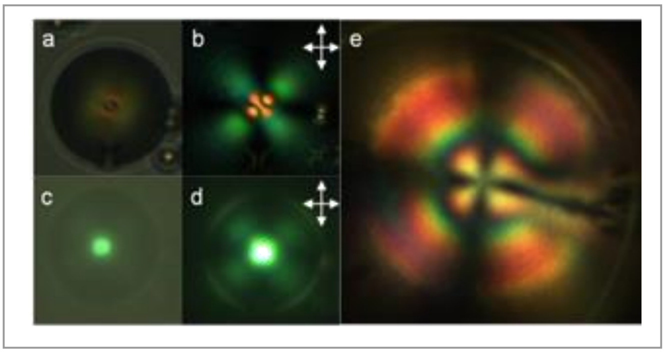

Fig. 4 Polarised optical microscopy images (x40) of Green reflective particles in Transmission a) without polarisers, b) between cross-polarisers and in Reflection c) without polarisers and d) between crossed polarisers. e) Infrared reflective particles between crossed polarisers.

Between crossed-polarisers, the optical texture observed corresponds to a radial distribution of the helicoidal axes due to a degenerate parallel anchoring, a model which was recently proposed by Zumer et.al..[2] Without polarisers, particles showed the so-called hedgehog defect on the top and a disclination line going from the centre to the border of the particle (Figure 4a). As any cholesteric system the reflected wavelength value is dictated by the chiral content and particles reflecting in any area of the spectrum can be produced by the reported method (Figure 4e).

The elimination of light-scattering is very important in terms of clarity of reflection and preservation of polarisation of the reflected and transmitted light. Light-scattering can be suppressed by matching the average refractive index of the particles with the refractive index of system in which they are embedded. The average refractive index of the particles was estimated by refractive index matching with different solvents and by ellipsometry on isotropic films with the same formulation as the particles. Both methods revealed an approximate average refractive index value of 1.59. The negative effect of the light-scattering on the reflection is shown in (Figure 5) where a dispersion of red particles looks white when dispersed in dodecane (n = 1.42) or red when dispersed in quinoline (n = 1.63). The reflectivity of dispersions with 0.5%wt. particle content in toluene was analysed by a UV spectrophotometer attached to an integrating sphere (x-Rite colour i5) (Table 1, Figure 6). ChRMPs reflecting in the blue, green and beginning of the red area of the visible spectrum were chosen for collecting the reflection spectra. Toluene was chosen due to its transparency and similarity of the refractive index (n = 1.49). Reflectivity values between 25-23% were obtained for each sample without polarisers. A broadband reflective dispersion in toluene with a 0.5%wt. particle content was prepared by mixing blue, green and red particles in a 1:1:1 ratio. Immediately after blending the particles the reflection of the new dispersion turned into grey which matches the silvery effect or mirror-effect of broadband cholesteric films reflecting the Visible area of the spectrum (Figure S9). The collected spectrum was based on the sum of the previous spectra corresponding to the single colour reflective dispersions.

Table 1. Optical data of 0.5%wt. ChRMPs based dispersions in toluene.

Dispersion	ʎmax [nm]	R [%] [a)]
Blue	430	25.2
Green	560	23.0
Red	600	24.0
R:G:B	440, 590	18.0, 18.4

a) Reflectivity.

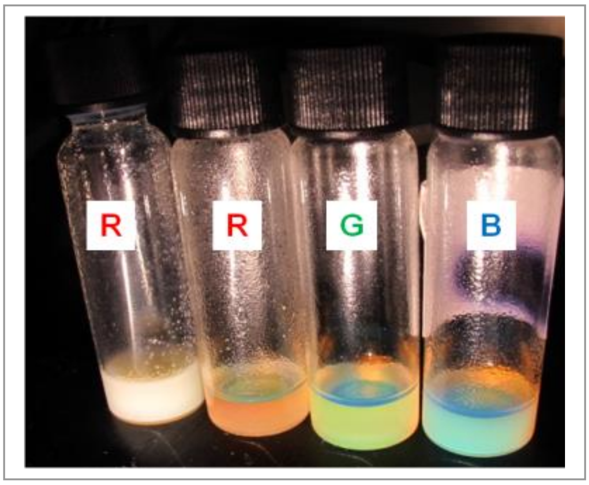

Fig. 5 .From left to right picture of: red (R) ChRMPs dispersed in dodecane. Red (R), green (G) and blue (B) Ch RMPs dispersed in quinoline.

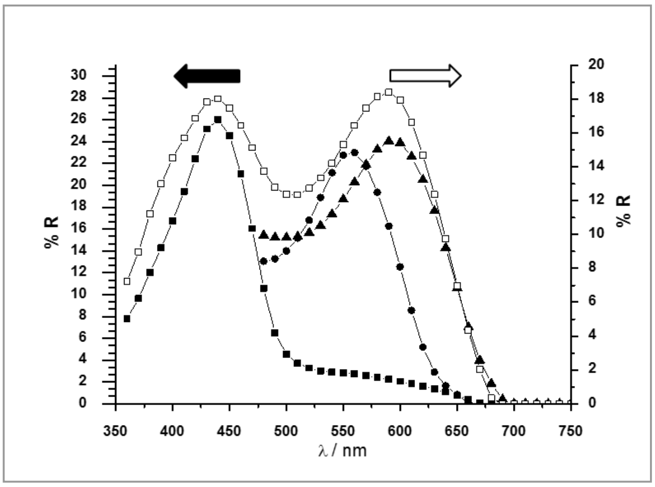

Fig. 6 Reflection of blue (black squares), green (black dots), red (black triangles) and RGB 1:1:1 blend (hollow squares) dispersions in toluene.

The latter result points out the high versatility of this particulate based reflecting system which makes it very easy to tune the reflection band from a single colour to a broadband-like reflection by mixing particles with their selective Bragg-reflection located at different wavelength values.

Solvent responsive particles were produced by lowering 15% the cross-linker content. Particles were stable enough for forming stable dispersions but at the same time the cross-link density was low enough for being permeable to different solvents causing a reversible elongation of the helicoidal axis when increasing the polarity of the solvent (Figure 7).

Cholesteric Reactive Mesogen Particles based Films

Planar alignment is the most favourable situation for reflective films based on cholesteric liquid crystal polymers. In order to arrange the molecules with their long-axes parallel to the substrate, the use of alignment layers and / or alignment additives is required.[26] Due to the fact that each particle is a micro domain with a very well defined alignment independent from its neighbour, alignment layers or alignment additives are not required for producing the films.

Coatable ChRMPs dispersions were prepared by mixing 0.05g of particles per millilitre of Acrifix9019. Films were produced by spin-coating on raw glass the latter dispersions at two different spin-speeds for 30 seconds. Particles were chosen to reflect light in the green area of the visible spectrum, which means red light was transmitted through the film (Figure S10). The binder was chosen in terms of transparency in the visible area of the spectrum but, as in the case of toluene, a perfect refractive index matching was not present (n_{binder} = 1.49). The reflectivity measurements were carried out by using x-Rite colour i5 spectrophotometer. Results are summarised in the following table (Table 2, Figure S11). Film A spin-coated at lower spin-speed than film B exhibited higher reflectivity value and higher particle content.

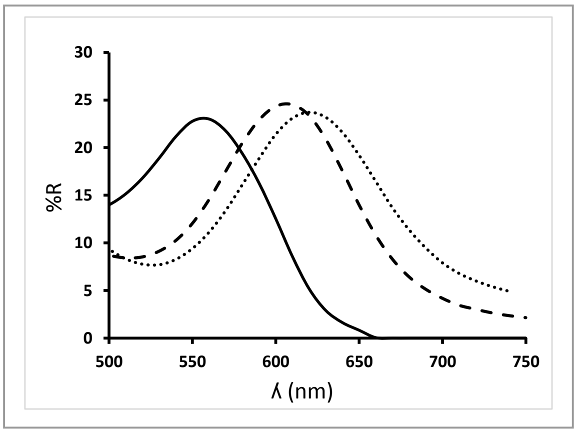

Fig. 7 Reflection spectra of particles with 15%wt. less cross-linker in toluene (solid line), 1,2-dichlorobencene (dashed line) and quinoline (dotted line).

Table 2. Size and Optical Data of ChRMPs based dispersions.

Film	Spin Speed [rpm]	Thickness [µm]	ʎmax [nm]	R [%] a)
A	80	~10	540	16.6
B	300	-b)	540	5.2

a) Reflectivity. b) Agglomerate of particles.

In terms of film morphology, the film A exhibited a homogenous distribution of the particles roughly based on a bilayer system where particles are almost completely covered by the binder (Figure 8). As a consequence, the surface of the film was not smooth and a rough thickness of 10µm was measured. The latter thickness value is in agreement with the bilayered structure of 5 micron-sized particles observed by SEM, indicating that particles are not swelled by the binder. By contrast, film B is based on agglomerates of particles linked to each other by the binder. The latter results pointed out the fact that particulate coatings are based on the concept of distributing particles along a given substrate. As a consequence, for a given system and conditions, the overall reflectivity is directly related to the particle content. In order to improve the coating quality we opted for doctor blading coating technique. Also, another binder based on epoxy resin with a refractive index similar to the refractive index of the particles was used. A film was produced by coating one third of the glass substrate with particles dispersed in toluene solution and the rest of the glass substrate with particles dispersed in the epoxy resin (19%wt. ChRMPs, 33%wt. toluene and 48%wt. epoxy resin). The same effect observed in Figure 5 was present in the case of films, and two clear areas were observed. A region with net particles did look white and non-reflection was observed by the naked eye due to the high light-scattering. However, in the area coated with the epoxy resin a clear reflected colour was observed due to the better refractive index match between particles and binder (Figure 9a). A closer view of the effect was observed by POM. Particles were clearly observed with very dark Becket lines in the area of the film without binder (Figure 9b) by contrast, almost non-visible particles in the epoxy resin area were observed (Figure 9c). Reflection spectra for both areas shown clearly the negative effect of the light-scattering in the reflection (Figure 9d). Finally, the extremely wide viewing-angle of a particulate film was observed by the naked eye when comparing the on-axis and off-axis reflectivity. As a comparison, the on-axis and off-axis reflection of a planar film, coated on raw glass without aligning additives, was also observed in order to check the viewing-dependent behaviour and the quality of the film.

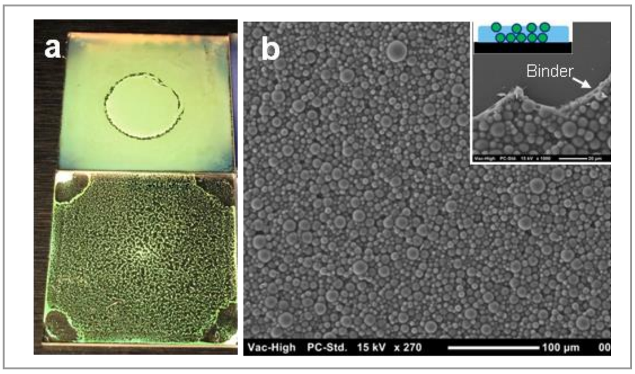

Fig. 8 a) Top film: film A; Bottom film: film B. b) SEM picture of film A. The inset shows the edged-morphology of film A.

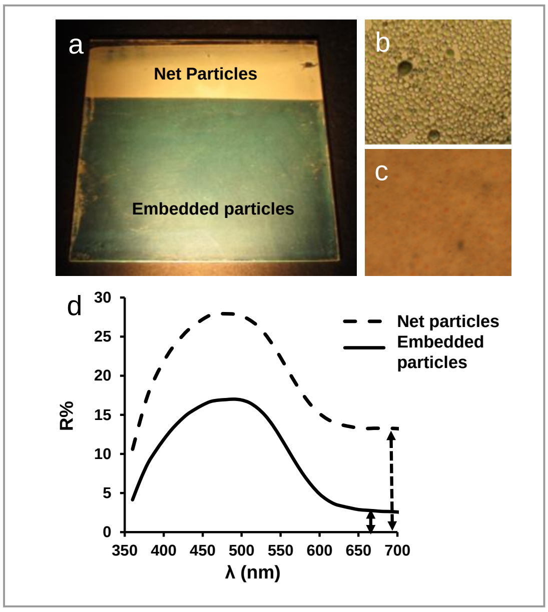

Fig. 9 a) Film containing net particles and particles embedded in an epoxy resin. b) POM image of net particles x20. c) POM image of particles embedded in epoxy resin x20. d) Reflection spectra for area of film with net particles (dashed line) and embedded particles in epoxy resin (solid line).

The latter planar cholesteric film shifted its reflection from green (on-axis) to blue (off-axis). In clear contrast, the particulate film kept the blue reflection independently of the vision angle (Figure 10). In terms of film quality, planar film resulted in a non-homogeneous surface with several dewets. Pointing out the fact that, in clear contrast to ChRMPs based films, high quality reactive mesogens based cholesteric films require aligning additives and / or alignment layers. An example of high-quality planar film coated on rubbed polyimide-glass (rubbed PI glass) is shown in the supporting information (Figure S12). It is worth mentioning that, so far, and due to deficiencies in terms of film making and binders used, the reflection exhibited by particulate films is lower than a well-oriented cholesteric films but the wide viewing-angle is an attractive feature which might compensated the lower reflection in specific applications.

Conclusions

An innovative first screening for producing reflective films using reactive mesogen based cholesteric particles is presented. The synthesis has been optimised for producing the particles with high batch-to-batch reproducibility. Reflective properties of the droplets are locked after its polymerisation and exhibit high thermal and solvent stability. By reducing the cross-linker content is possible to produce solvent responsive particles, which reversibly shift of the reflection depending on the polarity of the surrounded media. Multicoloured reflective systems by mixing different reflective particles has been proved and opens a good opportunity to produce white reflectors for brigtheness enhancement applications in a very easy and straightforward way. Embedding ChRMPs in a suitable binder without using

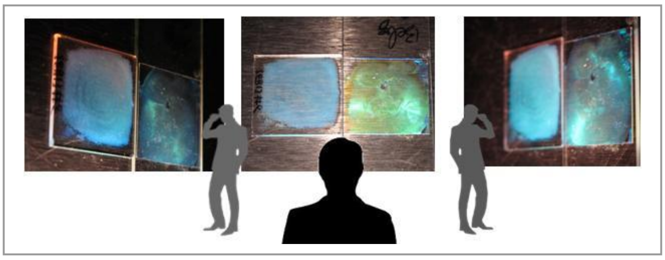

Fig. 10 On-axis (centre) and off-axis (edges) pictures of particulate film con-taining blue ChRMPs and planar green cholesteric film coated on raw glass. POM imagen of the particulate blue film (x40).

aligning promoters or surface energy modification steps on substrates, is sufficient for producing the films. Finally, it is remarkable that the very wide viewing angle reflection exhibited by the particles, which is a very valuable feature, avoids the usual colour leakage observed in conventional colour filters based on cholesteric liquid crystals.

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Novel approach to producing cholesteric mono- or multi-wavelength reflective systems which drive the reflection by mixing isolated Bragg-reflectors is presented.