Chirality transfer and stereo-selectivity of imprinted cholesteric networks

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Imprinting of cholesteric textures in a polymer network is a method of preserving a macroscopically chiral phase in a system with no molecular chirality. By modifying the elastic properties of the network, the resulting stored helical twist can be manipulated within a wide range since the imprinting efficiency depends on the balance between the elastics constants and twisting power at network formation. One spectacular property of phase chirality imprinting is the created ability of the network to adsorb preferentially one stereo-component from a racemic mixture. In this paper we explore this property of chirality transfer from a macroscopic to the molecular scale. In particular, we focus on the competition between the phase chirality and the local nematic order. We demonstrate that it is possible to control the subsequent release of chiral solvent component from the imprinting network and the reversibility of the stereo-selective swelling by racemic solvents.

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I. INTRODUCTION

Since its first discovery in the middle of the 19 century by Pasteur [1] and attempts on mathematical abstraction by Kelvin [2], chirality fascinates the scientific community across the disciplines. The nature appears to be inherently chiral. From the atomic scale with asymmetric carbon, to much larger length scales – like our hands and up to spiral galaxies, all have the same common feature of lacking the inversion symmetry, while not characterized by any vector (dipolar) property. In other words, many natural objects are non-superimposable with their mirror image and define a pair of opposite handedness, right and left. It is important to realize that handedness is not an absolute concept; its quantitative characteristics depend on the property being observed [3, 4], the origin of many questions and disagreements between different groups of results.

On a fundamental level, chirality is at the origin of a the “paradox of life”. In chemistry, molecules are equally present in their different forms, right and left-handed (this distinction, arbitrary in general, could be based on the rotation of plane polarization of a beam induced by the particular molecule under consideration). However, living system use only one stereo-form: amino acids constituting proteins are all left-handed and all nucleic acids of DNA and RNA are right-handed: a phenomenon of homochirality. Recently it has been demonstrated that a non-polarized light flow coupled with a parallel magnetically field induce one optical form from a racemic solution (ref). This magnetochiral anisotropy has revived a debate of the early sixties about the origin of homochirality.

“Wrong-handed” enantiomers can have dramatic consequences in all aspects of life. The left-handed sugar (L-glucose) tastes just as sweet as the right-handed one (D-glucose), but your body can’t use it as an energy source. Ibuprofen is one example of the chiral drugs widely used in pain relievers; the left-handed version is about four times as strong as the right-handed enantiomer. A famous medical disaster of 1960s involved the sedative thalidomide, initially produced with no chiral discrimination – it was later shown that one handedness of it had a poisonous effect. Today it is crucial for any pharmaceutical product to control the chirality, which implies the ability to synthesize selectively one enantiomer, or to separate the left- from the right-handed form and finally to quantify the stereo-selectivity. But how to separate a pair of opposite left- and right-handed molecules which differ only in a subtle way? This question represents a challenging problem. The main difficulty for stereo-selection is the weakness of molecular interaction sensitive to handedness. One of the main techniques in stereo-separation is column chromatography, in which a racemic mixture diffuses through a silica gel coated with a molecular layer of specific chirality: the two enantiomers of the mixture diffuse at slightly different rates due to the weak van der Waals attraction to the gel coating (due to the chiral corrections to high-order dielectric polarizability). New methods have been developed to measure such forces, for example, by detecting a difference in adhesion between an AFM tip coated with chiral molecules and the left- or right-handed substrate [5]. In all cases, the methods of stereo-selection have been based on interactions of individual molecules.

Recently a new approach has been suggested [6], based on the macroscopic phase chirality in topologically imprinted cholesteric networks [7]. Cholesteric order in liquid crystals results in a breaking of inversion symmetry of the nematic phase due to the presence of chiral molecules, e.g. a dopant in a mainly nematic material. As an immediate consequence, the director $n$ in cholesteric phase is spontaneously twisting in space, in a periodic helical fashion. The macroscopic helical pitch $p = 2\pi/q_0$ is inversely proportional to the concentration $\phi$ of the chiral dopant. The cholesteric phase frozen in the permanent polymer network (an elastomer or a gel) has been known for a long time [8, 9, 10, 11]. However, the topological imprinting of phase chirality is a new concept. In 1969, de Gennes was the first to suggest that chiral order can
be preserved by cross-linking a conventional polymer in a chira-
lly doped liquid crystal phase. Such a network would retain a
memory of the phase chirality even when the dopant is com-
pletely removed, leaving an internally stored helical twist in a
material without any molecular lack of symmetry. One has to
emphasize the difference with (common in biochemistry) ap-
proach to imprint a specific molecular property, such a site for
enzyme to attach – here the imprinted chiral property is on the
macroscopic scale and affects collective, coherent properties of
the system. Experimentally, elements of chiral imprinting
have been demonstrated in different polymer systems.

How to monitor the current state of phase chirality, the
helical pitch $p$ in the imprinted network? A traditional
method used in studies of liquid cholesterics is based on the
selective reflection of light at a certain wavelength.
However, in most techniques it is not chirality specific
(only explores the length scale matching between the hel-
ix and the light), and also requires very thin samples
with high optical quality – whereas in practice even the
best cholesteric rubbers never have such a quality. In
fact, recent studies has shown that one can generate the
bandgap for both right- and left- circular polarizations of
incoming light by only a slight mechanical deformation
of cholesteric elastomers. Instead we choose to
measure the optical rotation $\Psi$ (the angle of rotation of
plane polarization of light propagating along the helical
pitch), which is highly sensitive to any small variation of
the helical twist related to any change in chiral molecules
concentration $\phi$ in the network.

One particular property of imprinted network is the
stereo-selection between left- and right-handed molecules
from a racemic mixture which is used as a solvent. The
imprinted network will preferentially absorb and retain
chiral molecules fitting the handedness of its imprinted
macroscopic helix, in order to restore its initial helical
twist $q_0$. However, this stereo-selectivity effect is highly
non-trivial and influenced by several competing factors,
in particular by the local nematic order described by the
parameter $Q$. In a typical thermotropic liquid crystal
$Q$ depends on temperature difference $[T - T_c]$, with the
critical point $T_c$ a function of material composition, in
particular, the solvent content. As one adds a solvent
to a liquid crystalline gel, the magnitude of the local ne-
matic order parameter changes – usually decreases with
the overall solvent concentration $\phi$ in the network.
This results in a rapid change in local optical birefrin-
gence $\Delta n$ (affecting the optical rotation $\Psi$) and also the strength of
phase chirality (reducing the specific interaction with chiral
solvent). As soon as the material becomes isotropic,
i.e. loses its coherent cholesteric structure altogether, it
also loses the stereo-selectivity (at least to the accuracy
of our detection methods). In this paper we will explore
the ability of stereo-selective swelling of topologically im-
printed networks by studying the competition between
this local liquid crystalline order and the macroscopic
phase chirality. Finally, we will show by manipulating
the phase chirality (e.g. with temperature) it is possible
to control the subsequent release of chiral solvent com-
ponent from the imprinting network and the reversibility
of the stereo-selective separation.

II. IMPRINTING OF PHASE CHIRALITY

In theoretical analysis of chiral imprinting, Mao
and Warner (MW) have introduced a control parameter
that measures the (inverse) strength of imprinted helici-
ty in the polymer network, $\alpha = \sqrt{K_2/D_1q_0}$, where $K_2$
is the Frank (twist) elastic constant, $q_0$ is the heli-
x wavenumber at network formation (a measure of its
twisting power) and $D_1$ is the relative-rotation coupling
constant. If the network is formed with a large $\alpha$, it
would not be able to sustain its helical twisting when the
chiral dopant is removed, while at $\alpha \ll 1$ the more rigid
elastic network retains most of the imprinted helix. In
agreement with MW theory, we found that the stability
of topological imprinting of phase chirality is a function
of the chiral order parameter $\alpha$ (which can be altered
by modifying the crosslinking density which is directly
related to the elastic constant $D_1$).

At scales below the pitch length, cholesterics are an
amorphous uniaxial medium, described by the local ne-
matic order parameter $Q_{ij} = Q(T, \phi)(\eta_{ij} - \frac{1}{3} \delta_{ij})$, with
the director $n$ a periodic modulated function of coordi-
nates, in the ideal state rotating along a single axis $z$:
$n_x = \cos \theta, n_y = \sin \theta, n_z = 0$. In the ideal cholesteric
the azimuthal angle is $\theta = q_0 z$, with the correspond-
ing helical pitch $p_0 = \pi/q_0$, Fig. 4. This spontaneously
twisted director distribution can be due to the presence of
chiral molecules in the nematic polymer network during
its crosslinking. If, after crosslinking, the chiral dopant
then removed from this network (or replaced by an achi-
solvent), two competing processes occur: The Frank
energy penalty for the director twist, $\frac{1}{2} K_2 (n \cdot \text{curl} n)^2$,
demands the cholesteric helix to unwind; any remaining
twist causes the the rise of Frank energy. The local anchor-
ing of the director to the rubbery network, measured by
the relative-rotation coupling constant $D_1$, resists any
director rotations, thus acting to preserve the originally
imprinted helix. $D_1$ is proportional to the rubber mod-
ulus of the network and, through it, to the crosslinking

![FIG. 1: Spatial distribution of the director $n$ (shown here by
double-headed arrows) in an ideal cholesteric helix along the
macroscopic optical axis $z$.](image-url)
by the network. Very low crosslink density leads to low
\( \phi \) at low concentration of chiral solvent
\( \phi \), may or may not be accessed on de-swelling, depending on
\( \phi \) concentration at crosslinking is taken as
\( \langle \phi \rangle = 0.75 \), with
\( \phi = 0.105 \), (c) \( \phi = 1.75 \).

density. The free density energy is then given by the
competition of two effects:

\[
F = \int \frac{1}{2} \left[ K_2 \left( \frac{d}{dx} \theta - q \right)^2 + D_1 \sin^2(\theta - q_0 z) \right] dz \tag{1}
\]
with \( q \) the helical wave number that the current concentration of chiral solvent \( \phi \) would induce, \( q = 4\pi \beta \phi \), where \( \beta \) is the microscopic twisting power of the solute \[18\].

With its complete removal, \( \phi = 0 \) and \( q = 0 \), while the concentration at crosslinking is taken as \( \phi_0 \), with \( q = q_0 \), see Fig. \[2\].
MW have quantified the balance between these two opposing trends by introducing a parameter \( \alpha \), which in this case reads:

\[
\alpha = \xi [q_0 - q(\phi)], \quad \text{with} \quad \xi = \sqrt{K_2/D_1} \tag{2}
\]
the nematic rubber penetration length \[19\].
Note that both \( K_2 \) and \( D_1 \) are proportional to the square of local nematic parameter \( Q \), and so the length \( \xi \approx \text{const.} \)
The wave number \( q(\phi) \) in this definition is a linear function of chiral dopant concentration in the current state. The resulting classical problem of elliptical functions predicts that the helix coarsens and its period increases, as soon as \( \alpha \) increases past the threshold value of \( \pi/2 \).

Fig. \[2\] illustrates the model results by plotting the ratio \( \langle q \rangle /q_0 \), which is the relative number of remaining cholesteric phase inversions (helix periods).
After crosslinking at \( \{ \phi = \phi_0, q = q_0 \} \), on removing the chiral dopant the network initially is not affected until a critical value \( 4\pi \beta \phi^* = q_0 - 2/(\pi \xi) \) is reached. This critical point may or may not be accessed on de-swelling, depending on the values of \( \xi \) and \( q_0 \). The value of \( \langle q \rangle \) still remaining at \( \phi = 0 \) is the amount of topological imprinting of helix by the network. Very low crosslink density leads to low \( D_1 \), high \( \xi \) and the nearly complete unwinding of helices (loss of imprinting). A highly crosslinked network, leads to low \( \xi \) and, if \( \phi^* \leq 0 \), the complete retention of the original helix.

Our purpose in this paper is to explore the stereo-selectivity of polymer networks with no molecular chirality, but the phase chirality imprinted in the way described above. Stereo-selectivity leads to the imbalance \( \Delta \phi \) of chiral enantiomers swelling the network, which we monitor through the weight and shape of the sample (providing the data on total \( \phi \)), and the changes in optical rotation (giving direct access to \( \Delta \phi \)).

In order to interpret the results on optical rotation, we shall need to analyze two different regimes. Weak optical rotation (Faraday effect) of a solution with small chiral imbalance is a simple, unambiguously linear function of \( \Delta \phi \). However, when measuring the changes in the rotation of plane polarization of light passing through the cholesteric helix (whether imprinted or natural), a more delicate analysis is required. For this we need to revise the classical results of de Vries \[20, 21\] on the rotatory power of a cholesteric helix. The details of its application to this experimental problem are described in greater in our earlier work on cholesteric elastomers \[22\].
The main issue in a photonic bandgap system such as the cholesteric helix is the highly nonlinear rotation rate, whose value, and even sign, strongly depend on the relation between wavelength of light and the pitch \( p = \pi/q \).
The non-dimensional ratio \( \lambda' = \lambda_0/p \psi \), with \( \lambda_0 \) is the light wavelength and \( \psi \approx 1.68 \) the average refractive index, shows the position of the bandgap, see Fig. \[3\].

Importantly, in our system the initial cholesteric pitch \( p_0 \) was \( \sim 496 \text{nm} \) (labelled on the plot), so all the subsequent action (dopant removal and the subsequent chiral intake) takes place on the inside of the bandgap. To find the current value of pitch \( p \), which is affected by the amount of chiral dopant in the network, we need the approximate result derived in the earlier work, represented...
by the solid line in Fig. 3

\[ p \approx -\frac{\pi \Delta m^2 + \sqrt{\pi^2 \Delta m^4 + 16m^2 \lambda_0^2 (d\Psi/dz)^2}}{8m^2 (d\Psi/dz)} \]  

(3)

This interpolated model will serve us for the rest of this work, to help extracting the values of effective cholesteric pitch, as a measure of phase chirality, from the measured \( d\Psi/dz \) and the deduced \( \Delta m \).

### III. METHODS

#### A. Preparation of imprinted elastomers

The preparation of imprinted polysiloxane side-chain cholesteric elastomers follows the pioneering work of Kim and Finkelmann [23], which obtains monodomain cholesteric elastomers by uniaxial de-swelling during crosslinking. (Monodomain textures, with the cholesteric pitch uniformly aligned along the optical path, are essential for the study of giant optical rotation, see below). The mesogenic group (4’-methoxyphenyl 4-(buteneoxy)benzoate, MBB) and the crosslinker (1,4-di(11-undeceneoxy)benzene, di-11UB), both synthesized in-house, with the molar ratios of 9.2:0.8, 9:1, 8.5:1.5 and 8:2, doped with a fixed concentration (27% of total weight) of chiral compound (4-(2-methylbutyl)-4'-cyanobiphenyl, CB15), from Merck, were reacted with polymethylsiloxane chains in toluene, Fig. 4. After evaporation of the solvent and completion of crosslinking, cholesteric elastomers were obtained – with the same helical pitch \( \pi/q_0 \), irrespective of the crosslinking density.

In order to remove the chiral dopant CB15, the material is placed in a large volume of non-chiral solvent (acetone) leading to a diffusion of CB15 from the network in response to a concentration gradient.

![Chemical composition of the imprinted network](image)

**FIG. 4:** Chemical composition of the imprinted network.

#### B. Weak optical rotation

In order to topologically imprint the helical director in the liquid crystal elastomer, network has to be crosslinked in the presence of chiral dopant, which then is completely removed from the material, cf. Fig. 2. This has been achieved by placing the crosslinked gel, swollen with chiral dopant (in our case 27wt% CB15) in a large volume of nonchiral solvent (in our case – acetone). In response to a concentration gradient, chiral dopant diffuses from the network to the bulk of achiral solvent, inducing an small increase of its rotatory power \( \Psi \).

To detect very small variations of Faraday effect (optical activity) of a chiral molecules in dilute solution, a sensitive apparatus is needed. Our technique relies on the differential method. An incident polarized light (laser He-Ne, Melles-Griot) is decomposed, by using a polarizing cube beam splitters (Melles-Griot), into its two components of electric field vector: parallel \( E_\parallel \) or \( E_z \), (transmitted) and perpendicular \( E_\perp \), or \( E_y \), (reflected) to the plane of incidence. Finally, the angle of rotation \( \Psi \) of the plane polarization from its incident direction is measured with a differential detection by two photodiodes facing each other: \( \Psi = \arcsin \left( \frac{E_y - E_x}{E_y + E_x} \right) \) where \( E_{x,y} \) are the amplitudes of signal for the two orthogonally polarized beams (Fig. 5).

![Differential optical apparatus to measure the small optical rotation in bulk solvent, arising due to the diffusion of chiral dopant from the network. The signal is proportional to the difference between two photodiode readings, \( (E_\parallel - E_\perp) \).](image)

**FIG. 5:** Differential optical apparatus to measure the small optical rotation in bulk solvent, arising due to the diffusion of chiral dopant from the network. The signal is proportional to the difference between two photodiode readings, \( (E_\parallel - E_\perp) \).

#### C. Kinetics of dopant release

The variation in space and time of the chiral dopant concentration \( C \) in the bulk of the solvent, is due to the linear diffusion (without convection) between two parallel planes \( z \) (sample surface) and \( z + dz \) (beam path, \( dz \sim 1 \text{mm} \)). Figure 6 shows the evolution of \( \Psi \), for CB15 diffusing from networks with different crosslink density (8%, 10%, 15% and 20%) placed in an acetone bath. For all materials, the value of \( \Psi \) increases and saturates at \( \Psi \approx -1.5 \text{deg} \). For this ordinary isotropic Faraday effect \( \Psi = \varphi d \beta \), where \( \varphi \) is the solute concentration, \( d \) the optical path and \( \beta \) the twisting power of the solute. The negative absolute value of the angle corresponds to the clockwise rotation of polarization plane, which is the molecular property of CB15, and the phase property of...
the cholesteric helix at this wavelength.

However, the kinetics of this process is more complex than the simple Fickian diffusion, with the concentration \( \propto \exp(-z^2/4Dt) \). We find the initial “delay” time for the distance of 1mm of order 6-10min as in Fig. 5. After the given delay, the time to reach the saturation is of the same order of magnitude \( \sim 10\text{min} \) for all materials. If we assume the CB15 diffusion through a layer of acetone, after its release from the swollen gel, is a simple diffusion, then its constant can be estimated as \( D \sim (dz)^2/\tau_r \sim 5 \cdot 10^{-5}\text{cm}^2/\text{s} \) (a typical value for organic liquids of small molecules. The solid line on the plot illustrates the Fickian law for this diffusion constant, demonstrating the discrepancies: too long a delay and too fast onset of saturation after that in our experimental system. Clearly the observed kinetics is dominated by the gel de-swelling.

The characteristic times \( \tau_r \) of reaching the solvent saturation, obtained from Fig. 5, are plotted against the net-work cross-link density (Inset). The weak dependence of \( \tau_r \) on the crosslink density, and the values of time scales, indicate the role of gel de-swelling dynamics (resulting from the competition elasticity, diffusion and mixing, which only recently becomes better understood [24]. The small difference in CB15 concentration in the saturated solvent between the samples of different crosslinking den-

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![Fig. 6: Release of CB15 from the network for different crosslinker density (triangles: 20%; circles: 15%; crosses: 10%; squares: 8% crosslinking density). The small angle of rotation \( \Psi \) of plane-polarized light passing through the sample and the rotating analyzer is measured by its direct proportionality to the optical rotation \( \Psi \) from the imprinted network on which a droplet of solvent has been deposit.](image)

**D. Large optical rotation**

The rotation \( \Psi \) of plane-polarized light passing through a system with helically modulated birefringence, such as the cholesteric liquid crystal (whether natural or imprinted) can be determined experimentally by using a dynamical method [25] based on measuring the phase difference between the split parts of linearly polarized beam, one passing through the sample and the rotating analyzer, the other through the optical chopper (providing the reference signal to lock on), Fig. 4. In contrast to the differential method described above, this technique is suitable for measuring large rotation angles and

![Optical set-up for measuring large optical rotation](image)

**IV. IMPRINTING AND STERO-SELECTIVITY**

In this section we demonstrate the topological imprinting of the helix in networks from which the chiral dopant (CB15) has been completely removed. For this we detect
FIG. 8: Residual phase chirality –imprinted phase– after the complete removal of the CB15 chiral dopant, represented by the optical rotation rate $d\Psi/dz$. (a) Repeated flushes with acetone for the 10% crosslinked network show that the final value of $d\Psi/dz$ remains stable. (b) The amount of retained phase chirality is a function of the network crosslinked density.

The rotatory power $d\Psi/dz$ of the elastomer sample (prepared such that the axis of the imprinted helix is aligned perpendicular to the elastomer film, in the geometry shown in Fig. 1 and investigated in [17,23]). In a material with no intrinsic molecular chirality the rotatory power is determined only by the remaining cholesteric modulation of uniaxial dielectric constant in an imprinted helix. Figure 8(a) shows the rotatory power measured after repeated flushes of the elastomer (here, a 10% crosslinked sample) with an achiral solvent (acetone). In the periods when the gel is highly swollen, it is isotropic and we register no significant optical activity. On drying the solvent the liquid crystalline phase returns and its remaining imprinted helix produces a rotatory power $d\Psi/dz$, that is relatively constant after each swelling/drying cycle (which proves that there is no CB15 left in it after the first removal). The rotatory power of the imprinted helix is lower than the initial value in the natural cholesteric state in the presence of CB15 chiral dopant, which means that in this material the critical concentration $\phi^*_0$ is small but nonzero (such as for curve [a] in Fig. 2).

We performed the same experiment in the networks with different crosslink density (8%,10%,15% and 20%). The theory predicts that the remaining phase chirality, measured by the wave number $q_0$ of the imprinted helix, should increase as the parameter $\phi^*_0$ decreases and the nematic director is more strongly anchored to the elastic matrix. In agreement, we find that the amount of retained phase chirality decreases with the cross-link density, as shown in Fig. 8(b).

The resulting elastomer still retains a residual macroscopic phase chirality even with only centrosymmetric molecules left in the network. This frustrated system cannot be called a cholesteric liquid crystal, because this imprinted helix is not spontaneously formed, but is retained as a compromise between the untwisting trend of the nematic order and the rubber elastic resistance of the network to any internal deformation.

How the dry imprinted sample would behave in presence of a racemic mixture (a 50/50 proportion of left- and right-handed molecules)? One naturally expects, and the first attempt on theory indeed predicts, that the elastically frustrated network will have an “opportunity” to relieve its internal stress by allowing the helix to wind more. This opportunity will be offered to the liquid crystalline system if it preferentially absorbs the enantiomer with the “correct” twisting power, matching that of CB15 (which would act as a new chiral dopant, producing a new value of $q_0$).

From the results shown in Fig. 9 we observe that the solvent adsorption by the network affects strongly its macroscopic helical phase, depending mainly of the strength of the polymer matrix (cross-link density). The experiment is straightforward: the imprinted network is swollen in the racemic solvent (at a point in time labelled by the arrow in the plots) and then allowed to dry again. For densely cross-linked networks (15% and 20%, Fig. 9), the macroscopic helical phase given by the rotatory power $d\Psi/dz$ increases and saturates to a value close to what it was initially cross-linked in (cholesteric phase, C.P). This is the signature of stereo-selective swelling of imprinted networks. By selectively retaining a sufficient amount of chiral enantiomer, which agrees with the imprinted handedness of the network (and rejecting the molecules with opposite handedness), imprinted networks can return their residual helical pitch to the natural one corresponding to the cholesteric phase (in presence of CB15 dopant). In order to test this stereo-selective potential of imprinted networks, we did the same experiment with a stereo-neutral solvent. Figure 10 clearly shows no effect on the network as the repeated cycles in Fig. 8(a) also...
indicate. After the complete evaporation of the achiral solvent, the rotatory power $d\Phi/dz$ returns back to the initial value corresponding to the frustrated imprinted state.

For samples with weaker cross-linking, such as 8% and 10%, the value of $d\Phi/dz$ does not return back to the value corresponding to the cholesteric phase, reflecting a much less stereo-selective efficiency (Fig. 4). After swelling both weakly imprinted networks in a racemic mixture, the phase chirality monitored by $d\Phi/dz$ presents great instability and high amplitude of alternating helical pitch as the network “tries” to resolve its internal elastic frustration and the solvent content (this erratic behaviour is more pronounced for the 8% crosslinked sample). These erratic oscillations are qualitatively reproducible in other experiments and in repeated swelling cycles of the same sample. In fact, similar oscillations are observed in many situations of deswelling liquid crystalline polymer networks. Although no full theoretical explanation exists, this effect may be attributed to nonuniform distribution in space and time of coupled solvent density and local nematic order, as we discuss in the following section.

It appears that there is an optimal crosslinking density for imprinting, if one aims to maximize the stereo-selective effect, around 15% in our materials. Figure 4 suggests that at weaker linked networks the imprinting is clearly not strong enough to produce a sufficient and reliable chirality transfer and the resulting stereo-selectivity is small. However, in a more densely linked 20%xl network, although the imprinting is much more effective (nearly all of the original C.P. helix remains in the I.P.), the swelling capacity of it is not enough and the “window” of rotation rate gap between C.P. and I.P values is small.

V. HELICITY AND NEMATIC ORDER

What is the influence of the local nematic order $Q$ on the stereo-selective separation? As one adds a non-mesogenic solvent to a liquid crystalline network, even a small proportion of it reduces the local order parameter $Q$ and thus affects the chiral order parameter $\alpha$ defined by MW. Figure 11 shows the amount of solvent in such swollen imprinted networks, as it is allowed to dry. The results are shown for $\phi(t)$ in % value to the weight of the dry imprinted network. We specifically label the level of concentration, $\Phi' \sim 12\%$, at which the highly swollen isotropic gel first returns to the liquid crystalline state. One can tell, both visually and from the exponential fits, how much solvent is retained by each network. The saturation level at $t \to \infty$ is $\Delta\phi \approx 3.5\%$, $\Delta\phi \approx 4.5\%$, $\Delta\phi \approx 5\%$ and $\Delta\phi \approx 6\%$, for 8%, 10%, 15% and 20%xl networks, respectively. The 15%xl network swollen with a stereo-neutral solvent dries completely, $\Delta\phi = 0$.

In order to study the competition between the local nematic order $Q$, which is being diluted by solvents and disappears altogether above $\Phi'$, and the macroscopic phase chirality, we need to know how $d\Phi/dz(\phi)$ and $Q$ vary as function of $\phi$. We would prefer to measure the nematic order by the value of local optical birefringence $\Delta m(\phi)$, which are accurately in linear relation with each other, $\Delta m = \text{const} \cdot Q$. We can easily obtain the constant factor by calibrating this relation against a separate Xray scattering image, although we will not need this specifically in this paper.

However, it is nearly impossible to independently measure the local birefringence $\Delta m$, or equivalently, the local nematic order parameter $Q$, of an elastomer imprinted with a helical texture. The difficulty is the same as to measure $Q$ in a polydomain nematic. As a nearest compromise, we measure $\Delta m$ on a chemically similar aligned nematic liquid crystal elastomer (Fig. 4 aligned and crosslinked without CB15 dopant) and assume that its value and variation with $\phi$ would be the same in a cholesteric. It is not a totally unreasonable assumption: the degree of nematic order is very reliably
$Q \sim 0.5 \pm 0.1$ for most nematic liquid crystal materials (apart from main-chain polymers, which is not our case). The refractive indices depend more strongly on the molecular structure, varying between, say, 1.45 and 1.85 in different nematic materials. As a confirmation of our choice, the clearing temperature of this nematic material, $T_c \approx 90^\circ$C, is similar to that of the cholesteric elastomers.

In the following analysis, we concentrate on the 15% crosslinked network. Figure 12 shows the parallel results for the evolution with solvent content $\phi(t)$ of the rotation rate (a characteristic of the current helical pitch) and the birefringence (or, equivalently, the order parameter $Q$, obtained in the way described above). First of all, in order to avoid any problems on solvent concentration mapping, we brought the imprinted network to its isotropic state above the critical solvent concentration $\Phi^*$, which corresponds to the moment, when the sample first becomes isotropic when it is gradually swollen by the solvent ($\Phi^* = 12\%$ measured separately). Then the mapping of the measured $d\Psi/dz(t)$ and $d\Delta m(t)$ on the concentration dependence $\phi = \phi(t)$ has been obtained with an independent measurement the weight of the sample, initially in isotropic phase ($\phi > \Phi^*$) and gradually losing the solvent ($\phi \rightarrow 0$), Fig. 11.

Although the results presented in Fig. 12 are too rich for us to interpret them fully, it appears that a second critical concentration of solvent can be defined, above which we start loosing the underlying local order reducing the strength of the imprinted phase chirality and the stereo-selective separation is no longer effective. For a 15%xl network, this happens at $\phi \sim 7\%$. This demonstrates the importance of the local nematic order $Q$ (or $\Delta m$) on the stereo-selective potential as the racemic solvent swells the network. One can note the unexpected oscillation of $\Delta m$ as $\phi \rightarrow 0$. For the purpose of this paper, we do not discuss here this phenomenon further. However we hypothesize that these oscillations are caused by an instability of the solvent concentration gradient as

FIG. 12: Superposition of birefringence $\Delta m$ (solid line) and rotation rate $d\Psi/dz$ (circles) for a 15%xl imprinted network as function of decreasing concentration $\phi$, in a racemic environment.

one side of the sample is attached to a glass substrate (and its area conserved).

VI. REVERSIBILITY AND RELEASE

Is the process of stereo-selectivity reproducible and reversible? Figure 13 shows the evolution with time of the optical rotation $\Psi$ after addition of a second droplet ($\Phi^*$) of racemic solvent. In this second exposure the concentration of solvent taken into the network exceeds the critical concentration $\Phi^*$, at which the materials becomes isotropic. Accordingly the optical rotation rapidly drops to zero; $\Delta m = 0$ and the material loses its coherent helical structure altogether. On slow evaporation, as the concentration of solvent decreases, the local liquid crystallinity returns back. Then the imprinted phase chirality is restored and the stereo-selective separation can be effective again. As a result, some of the chiral component is retained again. The small difference between the resulting helical state in the two cases is certainly due to the difference in drying kinetics on the network coming back from the isotropic state, cf. Fig. 12.

The extraction of chiral molecules trapped into the network can be easily achieved by heating over the critical temperature $T_c$ of the isotropic state, as Fig. 14 indicates. After a slow cooling, the optical rotation $\Psi$ returns to the same level corresponding to the dry imprinted state $\langle q \rangle$, where no chiral entities are present in the network. Both components of the racemic mixture are able to evaporate with no hindrance, when the phase chirality of the imprinted helix is not present. Note that this phase chirality can be also mechanically tuneable if one stretches the swollen sample above the critical strain [27]. This would be a more controllable way for repeated cycling of stereo-selective separation.
FIG. 14: Release of chiral solvent from the 15%xl network by annealing. After the imprinted network is made to retain a portion of solvent, the sample is heated to above the clearing temperature, $T^* > 90^\circ$C. After annealing in the isotropic phase for about 2 hours, the sample is cooled to room temperature. The rotation returns $d\Psi/dz$ returns back to the value corresponding to the dry imprinted state.

VII. CONCLUSIONS

In this article we have reported on further details and physical effects produced by phase chirality imprinting in elastomer networks, as first described in [6, 7]. Although most theoretical arguments in support of the experimental findings are based on phenomenological continuum models, the underlying microscopic mechanism deserves some reflection. We call this phenomenon the chirality transfer. The imprinting of a cholesteric helix in a crosslinked network, even after removal of chiral dopants, is unambiguous and non-controversial. What is unusual, is that this macroscopic effect manages to influence chemical potential acting on individual chiral molecules of the racemic mixture. This is a universal action, quite independent on the relative chemical structure of the original dopant and the subsequent racemate. A molecular picture that we require to understand the transfer of macroscopic phase chirality down to the molecules of the racemic mixture involves a variable-shape construction in thermal motion. In our networks it is the strand of liquid-crystal polymer between the crosslinks. Its average shape in the nematic phase is a uniaxial ellipsoid, but in the presence of cholesteric helix the statistical distribution of chain segments becomes biased at a higher level, reflecting the additional breaking of inversion symmetry.

It interesting that another example of chirality transfer has recently been mentioned in the literature [24]. The new smectic liquid crystal phases (e.g. B4 and B7) of so-called “banana-shaped” or bent-core molecules are helically chiral on the submicron scale (similar to cholesterics) but the molecules have no molecular chirality [24]. The recent molecular model of this phenomenon involves the flexibility of the molecules, which allows them spend statistically more time in one of the chiral higher-energy conformations (while the ground state shape is non-chiral). Spectroscopic experiments appear to confirm this proposition of the chirality transfer down to the molecular level.

A spectacular property of imprinted helical networks is their capacity to selectively absorb and retain the component of a racemic solvent with the matching sense of chirality. It has obvious practical implications, however, this effect is sensitive to the variation of the local order parameter $Q$ during the network swelling by a solvent, since even small proportion of solvent would reduce $Q$ and affect the stereo-selectivity. By comparing the effects of an isotropic achiral solvent and a racemic mixture of two opposite chiral small-molecule components, we demonstrated how the imprinted elastomer selectively retains, after complete restoration of the local order, the fraction $\Delta\phi$ of guest chiral molecules in the network. It is important to emphasize that the chemical nature of the solvent used to test stereo-selectivity (p-Bromopentane) is completely different from the chiral dopant used originally to form the cholesteric phase (CB15). The imprinting of phase chirality and the subsequent chirality transfer are universal effects, working on the mean-field level and submicron length scales – and yet clearly affecting individual solvent molecules.

One other important practical characteristic of imprinted elastomers is that the phase chirality can be controlled by external factors (such as temperature, solvent or mechanical stress). Among other things, it allows the easy triggering of release of the chiral solvent component trapped into the network: by either bringing the imprinted elastomer into the isotropic phase, or by mechanically untwisting the helix. This process, which is reproducible and can then be reversed, makes the described stereo-selectivity phenomenon a practical possibility for many applications (no doubt the high surface area of a sponge of a fibrous mesh morphology would be beneficial in any such application). On the fundamental level, especially theoretically, much remains to be understood in the process of chirality transfer between the length scales.

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