Chirality transfer and stereoselectivity 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 elastic 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 a 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 a 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 discovery in the middle of the nineteenth 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, such as 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 nonsuperimposable 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 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 systems use only one stereo form: amino acids constituting proteins are all left-handed and all nucleic acids of DNA and RNA are right-handed.

"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 the body cannot 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 the 1960 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 selectively synthesize one enantiomer, or to separate the left- from the right-handed form and, finally, to quantify the stereoselectivity. But how to separate a pair of opposite left- and right-handed molecules that differ only in a subtle way? This is a challenging problem. The main difficulty for stereoselection 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). Methods have been developed to measure such forces, for example, by detecting a difference in adhesion between an antiferromagnetic (AFM) tip coated with chiral molecules and the left- or right-handed substrate [5]. In all cases, the methods of stereoselection have been based on interactions of individual molecules.

Recently, an 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 $\boldsymbol{n}$ 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 ϕ 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 [8–11]. However, the topological imprinting of phase chirality is a developing concept. In 1969, de Gennes suggested that chiral order can be preserved by cross-linking a conventional polymer in a chirally doped liquid-crystal phase [12]. Such a network would retain a memory of the phase chirality even when the dopant is completely removed, leaving an internally stored helical twist in a material without any molecular lack of symmetry. One has to emphasize the difference with an approach (common in biochemistry) to imprint a specific molecular property, such a site for the 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 [13,14].

How does one 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 (it only explores the length-scale matching between the helix 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 have shown that one can generate the band gap for both right and left circular polarizations of incoming light by only a slight mechanical deformation of cholesteric elastomers [15,16]. Instead, we choose to measure the optical rotation Ψ (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 molecule concentration ϕ in the network.

One particular property of an imprinted network is the stereoselection between left- and right-handed molecules from a racemic mixture, which is used as a solvent [7]. 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 stereoselectivity effect is highly nontrivial 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 the 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 nematic order parameter changes; it usually decreases with the overall solvent concentration ϕ in the network. This results in a rapid change in local optical birefringence Δm (affecting the optical rotation Ψ) 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 stereoselectivity (at least to the accuracy of our detection methods). In this paper, we will explore the ability of stereoselective swelling of topologically imprinted 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) that it is possible to control the subsequent release of the chiral solvent component from the imprinting network and the reversibility of the stereoselective separation.

II. IMPRINTING OF PHASE CHIRALITY

In a theoretical analysis of chiral imprinting [17], Mao and Warner (MW) have introduced a control parameter that measures the (inverse) strength of imprinted helicity in the polymer network, $\alpha=\sqrt{K_2/D_1}q_0$, where K_2 is the Frank (twist) elastic constant [18], q_0 is the helix wave number at network formation (a measure of its twisting power) and D_1 is the relative-rotation coupling constant [19]. If the network is formed with a large α, it would not be able to sustain its helical twisting when the chiral dopant is removed, whereas

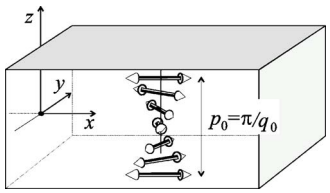

FIG. 1. (Color online) Spatial distribution of the director $\boldsymbol{n}$ (shown here by double-headed arrows) in an ideal cholesteric helix along the macroscopic optical axis z.

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 α (which can be altered by modifying the cross-linking 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 nematic order parameter $Q_{ij}=Q(T,\phi)\left(n_i n_j-\frac{1}{3}\delta_{ij}\right)$, with the director $\boldsymbol{n}$ a periodic modulated function of coordinates, in the ideal state rotating along a single axis z: $n_x=\cos\theta, n_y=\sin\theta$, and $n_z=0$. In the ideal cholesteric, the azimuthal angle is $\theta=q_0 z$, with the corresponding helical pitch $p_0=\pi/q_0$ (Fig. 1). This spontaneously twisted director distribution can be due to the presence of chiral molecules in the nematic polymer network during its cross-linking. If, after cross-linking, the chiral dopant is removed from this network (or replaced by an achiral solvent), two competing processes occur: the Frank energy penalty for the director twist, $\frac{1}{2}K_2(\boldsymbol{n}\cdot\mathrm{curl}\boldsymbol{n})^2$, demands the cholesteric helix to unwind; any remaining twist causes the rise of Frank energy. The local anchoring 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 modulus of the network and, through it, to the cross-linking density. The free density energy is then given by the competition of two effects

$$F=\int \frac{1}{2}\left[K_2\left(\frac{d}{dz}\theta-q\right)^2+D_1\sin^2(\theta-q_0 z)\right]dz, \qquad (1)$$

with q the helical wave number that the current concentration of chiral solvent ϕ would induce, $q=4\pi\beta\phi$, where β is the microscopic twisting power of the solute [18]. With its complete removal, $\phi=0$ and $q=0$, while the concentration at cross-linking is taken as ϕ_0, with $q=q_0$ (see Fig. 2). MW have quantified the balance between these two opposing trends by the parameter α, which in this case reads

$$\alpha=\xi[q_0-q(\phi)], \quad \text{with } \xi=\sqrt{K_2/D_1}, \qquad (2)$$

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 therefore, the length $\xi\approx$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 α increases past the threshold value of $\pi/2$.

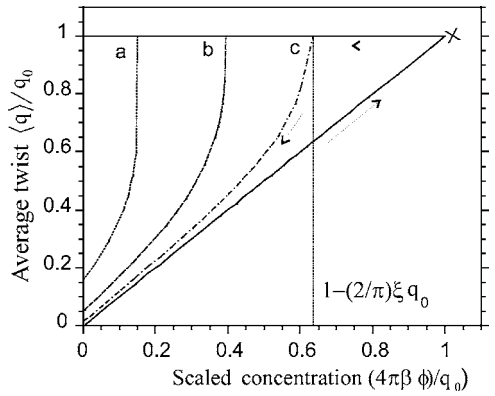

FIG. 2. Relative helical wave number as function of current chiral dopant concentration ϕ for the MW model. On increasing ϕ the wave number increases; the cross-linking occurs at $q=q_0$, a point labeled by the cross. On subsequent decreasing ϕ the strength of imprinting depends on parameter ξq_0: curves (a) $\xi q_0=0.75$, (b) $\xi q_0=1.05$, (c) $\xi q_0=1.75$.

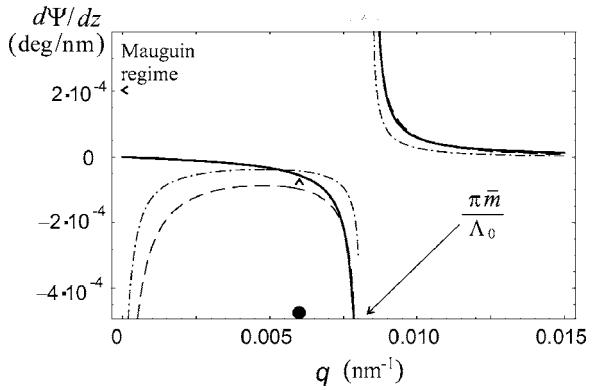

FIG. 3. The rate of optical rotation $d\Psi/dz$, as function of the helix wave number q. The solid line shows the interpolated result with correct limiting behavior, from [22]. The broken lines show the classical de Vries plots for decreasing local birefringence ($\Delta m=0.15$ and $\Delta m=0.05$). The band gap is at $\lambda'=1$, with a width decreasing with Δm. The dot marks the initial cholesteric pitch $p_0=\pi/q_0=496$ nm.

Figure 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 cross-linking 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 deswelling, depending on the values of ξ 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 cross-link density leads to low D_1, high ξ, and the nearly complete unwinding of helices (loss of imprinting). A highly cross-linked network leads to low ξ and, if $\phi^*\leqslant 0$, the complete retention of the original helix.

Our purpose in this paper is to explore the stereoselectivity of polymer networks with no molecular chirality, but the phase chirality imprinted in the way described above. Stereoselectivity 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 ϕ), 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 detail, in our earlier work on cholesteric elastomers [22]. The main issue in a photonic band-gap 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 nondimensional ratio $\lambda'=\Lambda_0/p\bar{m}$, where Λ_0 is the light wavelength and $\bar{m}\approx 1.68$ the average refractive index, shows the position of the band gap (see Fig. 3).

Importantly, in our system the initial cholesteric pitch p_0 was ~496 nm (labeled on the plot); thus, all the subsequent action (dopant removal and the subsequent chiral intake) takes place on the inside of the band gap. 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

$$p \approx -\frac{\pi\Delta m^2+\sqrt{\pi^2\Delta m^4+16\bar{m}^2\Lambda_0^2(d\Psi/dz)^2}}{8\bar{m}^2(d\Psi/dz)}. \qquad (3)$$

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 Δm.

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 deswelling during cross-linking. (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 cross-linker [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 cross-linking, cholesteric elastomers were obtained—with the same helical pitch π/q_0, irrespective of the cross-linking density.

In order to remove the chiral dopant CB15, the material is placed in a large volume of nonchiral solvent (acetone), lead-

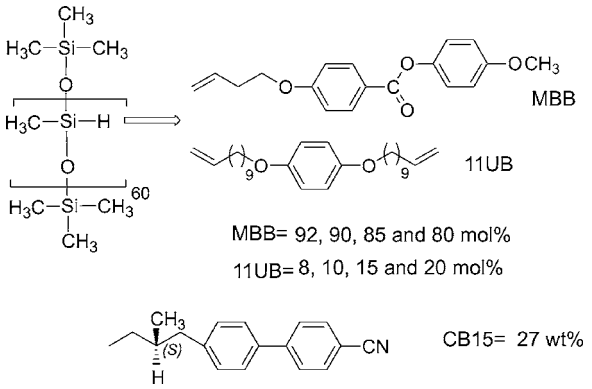

FIG. 4. Chemical composition of the imprinted network.

ing to a diffusion of CB15 from the network in response to a concentration gradient.

B. Weak optical rotation

In order to topologically imprint the helical director in the liquid-crystal elastomer, the network has to be cross-linked in the presence of a chiral dopant, which then is completely removed from the material (cf. Fig. 2). This has been achieved by placing the cross-linked gel, swollen with chiral dopant (in our case 27 wt. % 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 $\tilde{\Psi}$.

To detect very small variations of Faraday effect (optical activity) of 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 $E_{\|}$, or E_x, (transmitted) and perpendicular $E_{\perp}$, or E_y, (reflected) to the plane of incidence. Finally, the angle of rotation $\tilde{\Psi}$ of the plane polarization from its incident direction is measured with a differential detection by two photodiodes facing each other: $\tilde{\Psi}=\arcsin[(E_x-E_y)/E\sqrt{2}]$, where $E_{x,y}$ are the amplitudes of signal for the two orthogonally polarized beams (Fig. 5).

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, $dz\sim 1$ mm). Figure 6 shows the evolution of $\tilde{\Psi}$, for CB15 diffusing from networks with different cross-link density (8, 10, 15, and 20 %) placed in an acetone bath. For all materials, the value of $\tilde{\Psi}$ increases and then saturates. For this ordinary isotropic Faraday effect $\tilde{\Psi}=\varphi d\beta$, where φ is the solute concentration, d the optical path, and β the twisting power of the solute. The negative absolute value of the angle corresponds to the clockwise rotation of the polarization plane, which is the molecular property of CB15, and the phase property of the cholesteric helix at this wavelength.

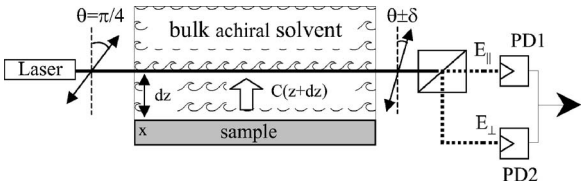

FIG. 5. Differential optical apparatus to measure the small optical rotation in bulk solvent, arising due to the diffusion of chiral dopant from the network. The signal is proportional to the difference between two photodiode readings, $(E_{\|}-E_{\perp})$.

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 1 mm of order 6–10 min, as in Fig. 6. After the given delay, the time to reach the saturation is of the same order of magnitude $\sim$10 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 $D\sim(dz)^2/\tau_r\sim 5\times 10^{-5}$ cm^2/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 an onset of saturation after that in our experimental system. Clearly, the observed kinetics is dominated by the gel deswelling.

The characteristic times τ_r of reaching the solvent saturation, obtained from Fig. 6, are plotted against the network cross-link density (inset). The weak dependence of τ_r on the cross-link density, and the values of time scales, indicate the role of gel deswelling dynamics (resulting from the competition elasticity, diffusion, and mixing, which only recently has become better understood [24]. The small difference in

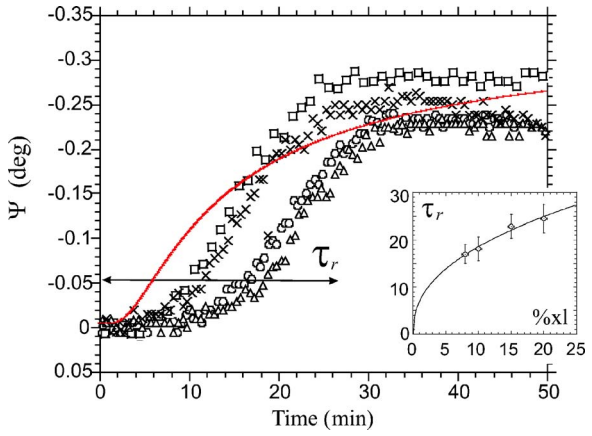

FIG. 6. (Color online) Release of CB15 from the network for different cross-linker density (triangles: 20%; circles:15% crosses: 10%; squares: 8% cross-linking density). The small angle of rotation Ψ is measured by its direct proportionality to the differential detection (E_x-E_y). The solid line shows the corresponding Fickian diffusion dynamics. Inset: Variation of the released time τ_r with cross-linker density; the line (a square-root fit) is only a guide to the eye.

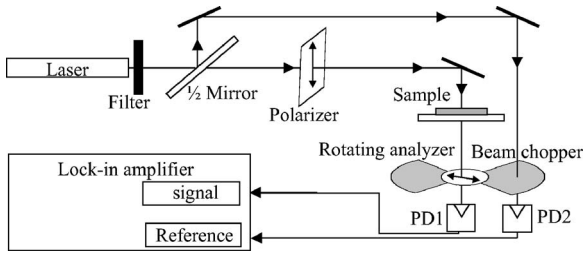

FIG. 7. Optical setup for measuring large optical rotation is based on the rotating analyzer to measure the optical rotation Ψ from the imprinted network on which a droplet of solvent has been deposited.

CB15 concentration in the saturated solvent between the samples of different cross-linking density is likely to be due to the differences in corresponding constants controlling these effects.

D. Large optical rotation

The rotation Ψ 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 [25,26] 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. 7). In contrast to the differential method described above, this technique is suitable for measuring large rotation angles and

The laser beam (He-Ne laser, $\lambda_{laser}=633$ nm, 30 mW, from Melles-Griot) is split by a 1/2-mirror. The straight part is polarized, passes through the sample, and then through the analyzer rotating at a fixed frequency ~ 16 Hz, then entering a detector. The sinusoidal signal is recorded with its phase determined by the rotation through the sample. The other part of the beam is sent around and through the chopper paddles mounted on the same rotating disk. This stepwise signal provides the reference, and the phase difference $\Delta\Theta$ between the two beams is measured by a whole number of periods with a lock-in amplifier (Stanford Research) and corresponds directly to the optical rotation Ψ from which the effective cholesteric pitch $\langle p \rangle$ is then calculated. The sample is deposited onto a glass coverslip, and a solvent droplet of known volume $(10\mu l)$ is placed on it, with the beam spot through the middle. Finally, the conversion of the raw rotation angle Ψ into the relevant rotatory power $d\Psi/dz$ is obtained by measuring, independently, the thickness variation of the network with the solvent concentration ϕ. This can be achieved by simply measuring the weight of the swollen imprinted network as function of time t from its isotropic state $(t=0)$ to $t \to \infty$, since its area is conserved in the x-y plane and would only change of thickness along z as function of ϕ by $\gamma_{z(\phi)}=(1+\phi)$.

The solvents used for swelling the dry imprinted network *in situ* were, respectively, toluene:hexane mixture (achiral solvent, ratio 1:6, from Acros) and 2-Bromopentane (racemic mixture of right and left isomers, from Acros).

IV. IMPRINTING AND STEREOSELECTIVITY

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 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 [15,23]). 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% cross-linked sample) with an achiral solvent (acetone). In 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 ϕ^* is small but nonzero (such as for curve [a] in Fig. 2).

We performed the same experiment in the networks with different cross-link density (8, 10, 15, and 20 %). The theory predicts that the remaining phase chirality, measured by the wave number q of the imprinted helix, should increase as the parameter ξq_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 would the dry imprinted sample behave in the presence of a racemic mixture (a 50/50 proportion of left- and right-handed molecules)? One naturally expects, and an early attempt on theory [6] 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 chiral dopant, producing a value of q_0).

From the results shown in Fig. 9, we observe that the solvent adsorption by the network strongly affects its macroscopic helical phase, depending mainly on the strength of the polymer matrix (cross-link density). The experiment is straightforward: the imprinted network is swollen in the ra-

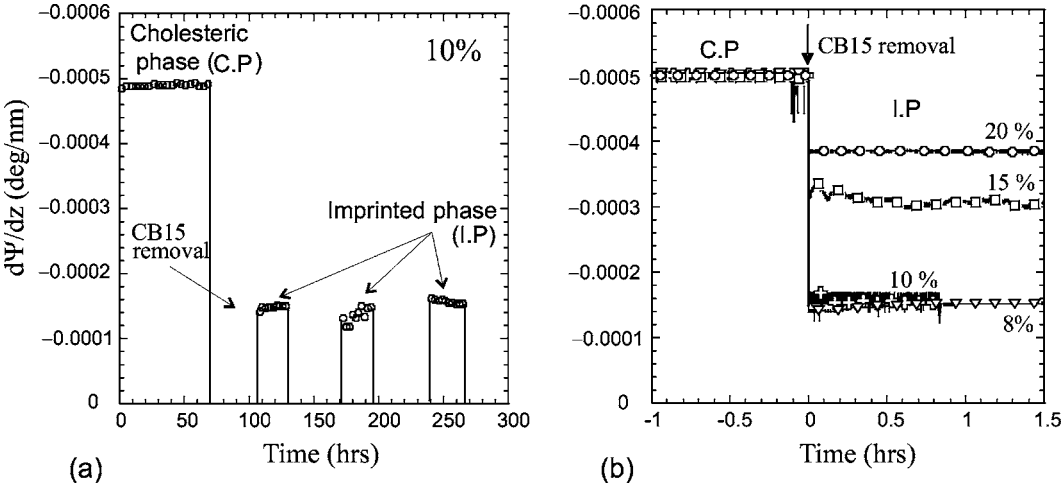

FIG. 8. Residual phase chirality—imprinted phase—after the complete removal of the CB15 chiral dopant, represented by the optical rotation rate $d\Psi/dz$. (a) Repeated flushes with acetone for the 10% cross-linked network show that the final value of $d\Psi/dz$ remains stable. (b) The amount of retained phase chirality is a function of the network cross-linked density.

cemic solvent (at a point in time labeled 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 (CP)]. This is the signature of stereoselective 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 the presence of CB15 dopant). In order to test this stereoselective potential of imprinted networks, we did the same experiment with a stereoneutral 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 $d\Psi/dz$ returns to the initial value corresponding to the frustrated imprinted state.

For samples with weaker cross-linking, such as 8 and 10 %, the value of $d\Psi/dz$ does not return to the value corresponding to the cholesteric phase, reflecting a much less stereoselective efficiency (Fig. 9). After swelling both weakly imprinted networks in a racemic mixture, the phase chirality monitored by $d\Psi/dz$ 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 behavior is more pronounced for the 8% cross-linked 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

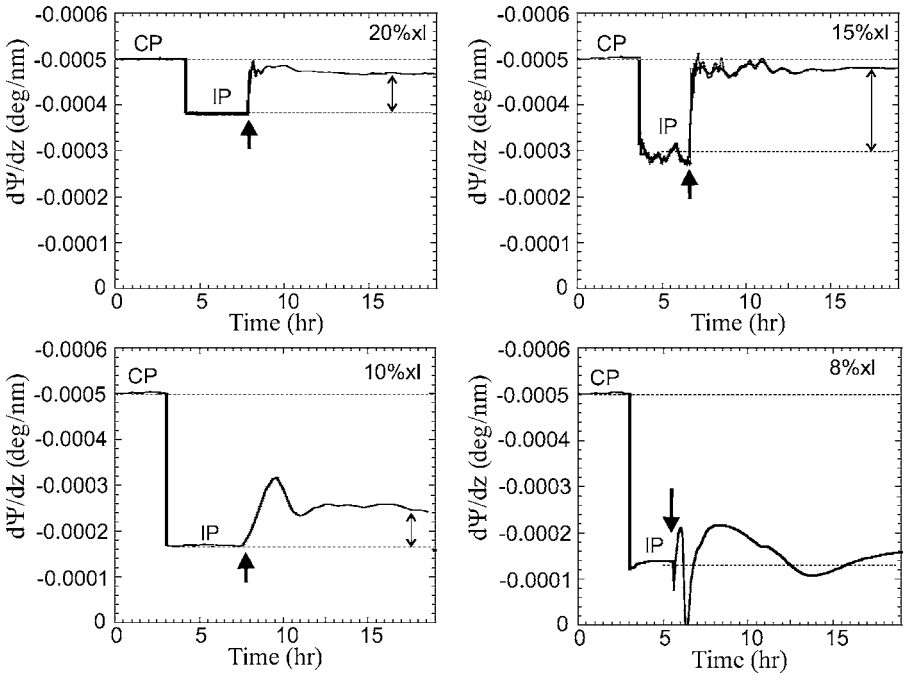

FIG. 9. Variation of the rotatory power $d\Psi/dz$ for 8, 10, 15, and 20 % cross-linked networks in their imprinted state. At time $t=0$, the racemic mixture is deposited on the dry imprinted (IP) samples (indicated by arrows). For both 15 and 20 % cross-link density networks, the initial helical pitch [cholesteric phase (CP)] is restored almost completely by stereoselective absorption of chiral molecules. For lower cross-link densities (8 and 10 %), the variation of $d\Psi/dz$ presents a more erratic behavior.

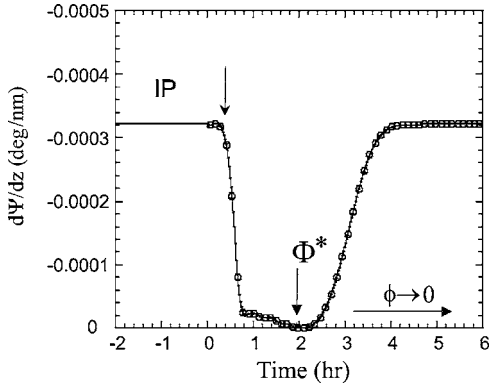

FIG. 10. Variation of the rotation rate $d\Psi/dz$ for a 15% cross-linked imprinted network swollen by an achiral solvent, which is then allowed to dry. Φ^* is the critical solvent concentration below which the nematic order returns to the system (see Sec. V).

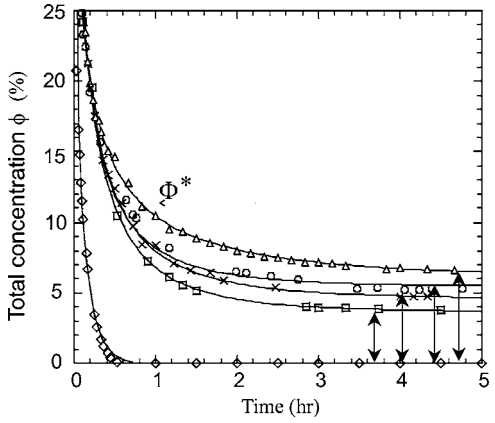

FIG. 11. Decreasing solvent content $\phi(t)$ on drying imprinted networks with different cross-link density – 8% xl (squares), 10%xl (crosses), 15%xl (circles) and 20%xl (triangles). For comparison, the diamond symbols show the drying of the 15%xl network after swelling in the achiral solvent. Φ^* labels the concentration at which the liquid crystal order reemerges in the system; solid lines are the exponential fit with and without the saturation constant at $t=\infty$ for different cases.

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 Sec. V.

It appears that there is an optimal cross-linking density for imprinting, if one aims to maximize the stereoselective effect, ~15% in our materials. Figure 9 suggests that at weaker linked networks the imprinting is clearly not strong enough to produce a sufficient and reliable chirality transfer, and the resulting stereoselectivity is small. However, in a more densely linked 20%xl network, although the imprinting is much more effective (nearly all of the original CP helix remains in the IP), the swelling capacity of it is not enough and the "window" of rotation rate gap between CP and IP values is small.

V. HELICITY AND NEMATIC ORDER

What is the influence of the local nematic order Q on the stereoselective separation? As one adds a nonmesogenic 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 α 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 percent 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 stereoneutral 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 Φ^*, and the macroscopic phase chirality, we need to know how $d\Psi/dz(\phi)$ and Q vary as a function of ϕ. 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, $\Delta m = \text{const} Q$ [18]. We can easily obtain the constant factor by calibrating this relation against a separate x-ray-scattering image, although we will not need this specifically in this paper.

However, it is nearly impossible to independently measure the local birefringence Δm, 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 the nearest compromise, we measure Δm on a chemically similar aligned nematic liquid-crystal elastomer (Fig. 4, aligned and cross-linked without CB15 dopant) and assume that its value and variation with ϕ 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, $T_c \approx 90\ ^\circ\text{C}$, is similar to that of the cholesteric elastomers.

In the following analysis, we concentrate on the 15% cross-linked 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 Φ^* that 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 $\Delta m(t)$ on the concentration dependence $\phi=\phi(t)$ has been obtained with an independent measurement of the weight of the sample, initially in the isotropic phase ($\phi > \Phi^*$) and gradually losing the solvent ($\phi \to 0$), (Fig. 11).

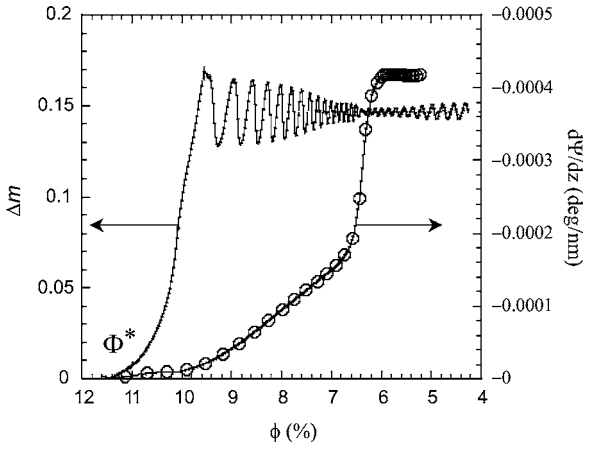

FIG. 12. Superposition of birefringence Δm (solid line) and rotation rate $d\Psi/dz$ (circles) for a 15%xl imprinted network as function of decreasing concentration ϕ, in a racemic environment.

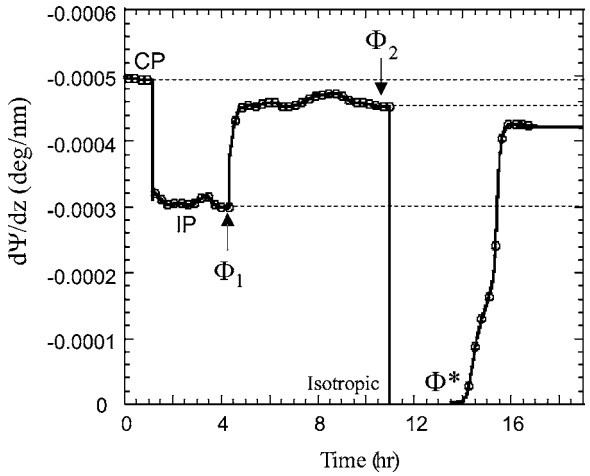

FIG. 13. Effect of high concentration solvent ($\phi > \Phi^*$) on a 15%xl imprinted network: Φ_1 and Φ_2 correspond, respectively, to the first (small) droplet and the second (large) droplet of racemic solvent deposited onto the sample.

Although the results presented in Fig. 12 are too rich for us to fully interpret, it appears that a second critical concentration of solvent can be defined, above which we start losing the underlying local order, reducing the strength of the imprinted phase chirality, and the stereoselective 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 Δm) on the stereoselective potential as the racemic solvent swells the network. One can note the unexpected oscillation of Δm as $\phi \to 0$. For the purpose of this paper, we do not discuss this phenomenon further. However, we hypothesize that these oscillations are caused by an instability of the solvent concentration gradient as one side of the sample is attached to a glass substrate (and its area is conserved).

VI. REVERSIBILITY AND RELEASE

Is the process of stereoselectivity reproducible and reversible? Figure 13 shows the evolution with time of the optical rotation Ψ after addition of a second droplet (Φ_2) of racemic solvent. In this second exposure the concentration of solvent taken into the network exceeds the critical concentration Φ^* at which the materials become 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. Then the imprinted phase chirality is restored and the stereoselective 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 Ψ 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 also be mechanically tunable if one stretches the swollen sample above the critical strain [27]. This would be a more controllable way for repeated cycling of stereoselective separation.

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 re-

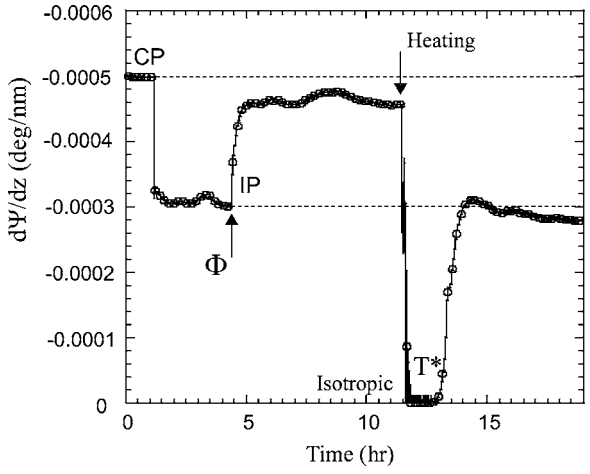

FIG. 14. Release of chiral solvent from the 15%xl network by annealing. After the imprinted network is made to retain a portion of solvent, the sample is heated to above the clearing temperature, $T^* > 90\ ^\circ$C. After annealing in the isotropic phase for about 2 h, the sample is cooled to room temperature. The rotation returns $d\Psi/dz$ returns back to the value corresponding to the dry imprinted state.

flection. We call this phenomenon the chirality transfer. The imprinting of a cholesteric helix in a cross-linked network, even after removal of chiral dopants, is unambiguous and noncontroversial. 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 cross-links. 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 is interesting that another example of chirality transfer has recently been mentioned in the literature [28]. The 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 [29]. The recent molecular model of this phenomenon involves the flexibility of the molecules, which allows them to spend statistically more time in one of the chiral higher-energy conformations (while the ground state shape is nonchiral). 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 because even a small proportion of solvent would reduce Q and affect the stereoselectivity. 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 stereoselectivity (*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 stereoselectivity 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.

ACKNOWLEDGMENTS

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