Stereo-Selective Swelling of Imprinted Cholesteric Networks

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Molecular chirality, and the chiral symmetry breaking of resulting macroscopic phases, can be topologically imprinted and manipulated by cross-linking and swelling of polymer networks. We present a new experimental approach to stereo-specific separation of chiral isomers by using a cholesteric elastomer in which a helical director distribution has been topologically imprinted by cross-linking. This makes the material unusual in that is has a strong phase chirality, but no molecular chirality at all; we study the nature and parameters controlling the twist-untwist transition. Adding a racemic mixture to the imprinted network results in selective swelling by only the component of "correct" handedness. We investigate the capacity of demixing in a racemic environment, which depends on network parameters and the underlying nematic order.

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Because of the lack of inversion symmetry, chiral molecular objects are nonsuperimposable with their mirror image. A pair of opposite, left- and right-handed, isomers differs in shape only in a very subtle way, which results in small corrections to higher-order molecular polarizability. Although chirality was known as a phenomenon since the middle of the 19th century, the quantitative characterization of such a delicate physical property has been only achieved in the last decade [1,2]. It is now understood that handedness is not an absolute concept but depends on the property being observed; different scalar parameters describing chirality can have differing signs and can vanish at different points as an object is continuously deformed into its mirror image.

Chirality is a ubiquitous feature of the biological world. Many, if not most functions of fundamental living components rely upon their chirality. Thus the synthesis of a single enantiomer of a compound, or its separation from a 50/50 racemic mixture, is crucial for many practical applications—from pharmaceuticals, to food and cosmetics. This stereo-selection is always a difficult task, because the molecular interactions that are sensitive to its handedness are always very small. One of the main techniques in this field 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 (higher-order) van der Waals attraction to the gel coating.

Microscopic chiral constituents have a profound effect on the macroscopic structures they form, striking examples of which are common in liquid crystals [3]. The simplest liquid crystalline phase is the nematic, characterized by a long-range uniaxial orientational order of rodlike anisotropic molecules along a common director $\boldsymbol{n}$. Adding chiral molecules results in a cholesteric phase, with the director twisting in space in a periodic helical fashion, with the pitch inversely proportional to the concentration of chiral dopant. Analogous states with macroscopic "phase chirality" are found in blue phases and a variety of smectic liquid crystals. The coherent arrangement of molecular units on a macroscopic scale, such as the cholesteric helix, greatly enhances physical manifestations of chirality. For instance, the optical rotation (Faraday effect) of a solution of chiral molecules can be enhanced by up to 10^4 in a cholesteric phase generated by the same amount of chiral doping. It is attractive to utilize this macroscopic enhancement of normally weak chiral interactions.

In this Letter, we demonstrate the effect of stereo-selection between left- and right-handed molecules of a racemic mixture, achieved in a polymer gel network in which cholesteric order has been topologically imprinted by cross-linking. Cholesteric polymers and their networks have been known for a long time [4–7], however, the topological imprinting of phase chirality is a completely different concept. The network cross-linked in the cholesteric phase induced by a chiral dopant would retain a memory of chirality even when the dopant is completely removed, leaving an internally stored helical twist in a material with no chemical (microscopic) chirality. de Gennes was the first to suggest that chiral order can be induced by cross-linking a conventional polymer in a chiral liquid crystal phase [8]. Experimentally, elements of chiral imprinting have been demonstrated in different polymer systems [9,10]. A continuum theory for chiral imprinting in nematic elastomers formed in a chiral environment has been developed by Mao and Warner (MW) [11], followed by their theoretical suggestion about stereo-selective swelling and chiral separation [12]. Qualitatively, the concept is simple: chiral dopant molecules leave a specific "trace," frozen-in by chemical cross-linking of polymer chains; on bringing in a racemic solvent, the component of correct handedness recognizes the trace and thus has a preference in swelling the network. However, the real problem is highly nontrivial and

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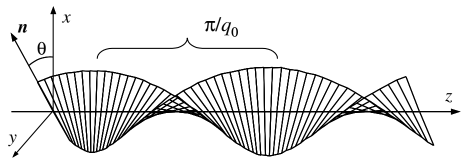

FIG. 1. Spatial distribution of the director ***n*** in an ideal cholesteric helix along the macroscopic optical axis z.

influenced by several competing factors. Our task here is to test the basic theoretical model and explore stereoselective interactions according to the handedness of the imprinted network.

Locally cholesterics are an amorphous uniaxial medium, described by the local nematic order parameter $Q_{ij} = Q(T, \phi)(n_i n_j - \frac{1}{3}\delta_{ij})$, with the director ***n*** a periodic modulated function of coordinates, in the ideal state rotating along a single axis z: $n_x = \cos\theta$, $n_y = \sin\theta$, $n_z = 0$. 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. The local anchoring of the director to the rubbery network, measured by the relative-rotation coupling constant D_1 [13], resists any director rotations, thus acting to preserve the imprinted helix. D_1 is proportional to the rubber modulus of the network and, through it, to the cross-linking density [14]. The free density energy is then:

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

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 [3]. With its complete removal, $\phi = 0$ and $q = 0$, while the concentration at cross-linking is taken as ϕ_0, with $q = q_0$. MW have quantified the balance between these two physical trends by introducing a chiral order parameter α:

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

the nematic rubber penetration length. Note that both K_2 and D_1 are proportional to the square of local nematic parameter Q, and so the length $\xi = \text{const}$. 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 $\pi/2$.

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 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 $\phi^* \leq 0$, the complete retention of the original helix.

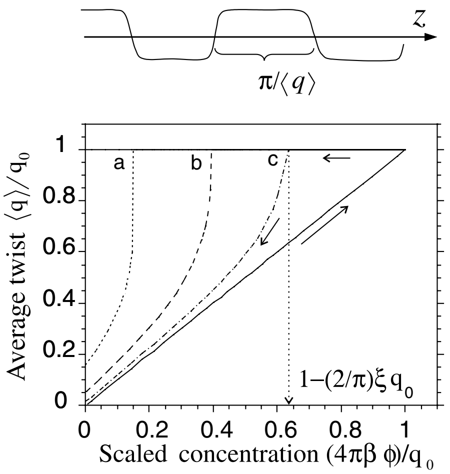

FIG. 2. Relative helical wave number as a function of chiral dopant fraction ϕ for the MW model. On increasing ϕ the wave number increases; the cross-linking occurs at $q = q_0$. On subsequent decreasing ϕ the strength of imprinting depends on parameter ξq_0: curves (*a*) $\xi q_0 = 0.75$, (*b*) $\xi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

It appears that the average pitch wave number $\langle q\rangle$ is the pertinent variable. The theoretical model has its strong and weak points, but the underlying physical effect is clear and universal. Our first task is to experimentally study the process of topological imprinting of chirality. Its measurement is possible due to the remarkable optical property of cholesterics: their giant optical rotation. The eigensolutions for electromagnetic waves propagating along z are superpositions of two circularly polarized plane waves of opposite signs [15]. Their phase difference gives the optical rotation Ψ in the medium, the rate of which can be related to the average pitch wave number $\langle q\rangle$ by the de Vries equation:

$$\frac{d\Psi}{dz} = -\langle q\rangle a^2\left\{4\left(\frac{\langle q\rangle\Lambda}{\pi\sqrt{\bar{\varepsilon}}}\right)^2\left[1 - \left(\frac{\langle q\rangle\Lambda}{\pi\sqrt{\bar{\varepsilon}}}\right)^2\right]\right\}^{-1}, \qquad (3)$$

where Λ is the wavelength of the incident light (He-Ne laser, 633 nm), $a = (n_e^2 - n_o^2)/(n_e^2 + n_o^2)$ is the dielectric anisotropy parameter (where in our material the extraordinary and ordinary refractive indices are, respectively, $n_e = 1.75$ and $n_o = 1.6$), and in zero-order approximation $\bar{\varepsilon} = \frac{1}{2}(n_e^2 + n_o^2)$ is the mean dielectric constant. For $\langle q\rangle = \pi\sqrt{\bar{\varepsilon}}/\Lambda$ a dispersion anomaly appears in the form of Bragg-like reflection [15]. In our case this anomaly would occur at $\langle q\rangle/\pi \approx (381\,\mathrm{nm})^{-1}$. In practice, we obtain the initial wave number of cholesteric state $q_0/\pi \approx (496\,\mathrm{nm})^{-1}$, which means that our range of measurements is always on the longer wavelength side of the point of divergence in Eq. (3).

Experimentally, the optical rotation Ψ can be determined using a dynamical method based on measuring the phase difference between the split parts of linearly polarized laser beam, one passing through the sample and the rotating analyzer, the other through the chopper (providing the reference signal to lock on). The phase between the two beams is measured by an integer number of periods and corresponds directly to the optical rotation Ψ, from which the parameter $\langle q\rangle$ is then calculated.

From the theory, we have seen that the robustness of chiral imprinting depends on the nematic penetration depth $\xi = \sqrt{K_2/D_1}$, which can be controlled by varying the density of cross-links in the network (affecting D_1). The preparation of imprinted polysiloxane cholesteric elastomers follows the pioneering work of Kim and Finkelmann [16], 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). 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. 3. 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) leading to a diffusion of CB15 from the network in response to a concentration gradient. The release of the chiral dopant is then determined by measuring the rotation of the polarization plane $\tilde{\Psi}$ of the bulk solvent with a differential detection: $\tilde{\Psi} = \arcsin[(E_x - E_y)/E\sqrt{2}]$ where $E_{x,y}$ is the signal amplitude for the two perpendicular polarizations. Figure 4(a) shows the evolution of $\tilde{\Psi}$ for elastomers with different cross-link density "washed" in a nonchiral solvent. For all materials, the value of $\tilde{\Psi}$ increases and saturates for $\tilde{\Psi} = -1.5$ deg (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 CB15). The characteristic time of dopant release is approximately the same for all elastomers and is $\tau \sim 20$ min, at room temperature, showing perhaps a slight increase with cross-link density.

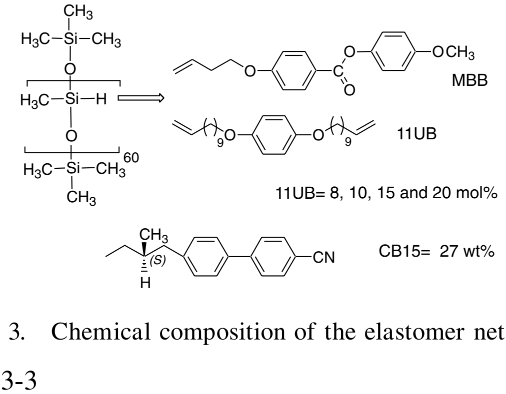

FIG. 3. Chemical composition of the elastomer network.

After drying, does the resulting elastomer still retain a residual macroscopic (phase) chirality with only centrosymmetric molecules left in the network? Figure 4(b) is the case for the network with 10% cross-linking, which shows that the average wave number remains nonzero after the "wash," $\langle q\rangle/\pi \approx (505\,\mathrm{nm})^{-1}$, although lower than the initial value in the presence of chiral dopant. Repeated flushes with acetone evidently do not have any further effect. We find the same initial wave number $q_0/\pi \approx (496\,\mathrm{nm})^{-1}$ for all elastomers, but the amount of retained phase chirality is a function of the cross-link density, see Fig. 5. As theory predicts, the remaining fractional wave number $\langle q\rangle/q_0$ increases as the parameter ξq_0 decreases and the director $\boldsymbol{n}$ is more strongly anchored to the network.

Now if the imprinted elastomer is brought in contact with a racemic mixture (a 50/50 proportion of left- and right-handed small molecules, 2-bromopentane, from ACROS), its natural wave number q_0 can be restored by selective absorption of chiral molecules which agree with the imprinted handedness of the network, and rejecting the molecules with wrong handedness. The experiment is straightforward: the imprinted network is swollen in the racemic solvent, and then allowed to dry again. With a stereo-neutral solvent, nothing happens with the network, as the repeated cycles in Fig. 4(b) indicate. Figure 5 shows that densely cross-linked networks (15 and 20%) are able to retain a sufficient amount of left-handed (S) component of the mixture to return their average cholesteric pitch to nearly the same level as they had before the CB15 removal: 496.9 and 496.6 nm, respectively. Networks with lower cross-linking density show less stereoselectivity. Elastomers with weaker cross-linking retain much less of the racemic solvent, returning their pitch to 499 for 10% and to 512 nm for 8% network. Note that in

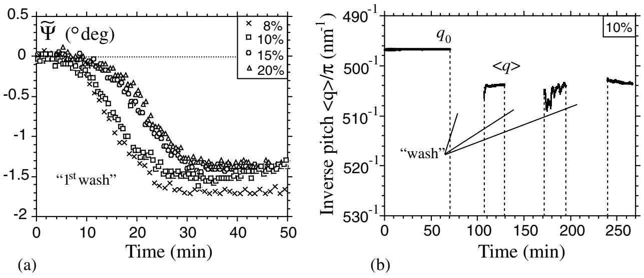

FIG. 4. (a) Chiral dopant release from the imprinted network into the "wash." (b) The effect of CB15 removal on the inverse helical pitch for the 10% cross-linked network.

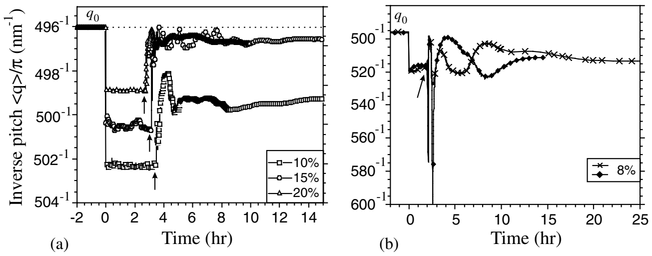

FIG. 5. The inverse cholesteric pitch of imprinted elastomers, $p^{-1} = \langle q \rangle / \pi$. The plots show the initial value at cross-linking, the imprinted plateau level of the dry network, and the change after exposure to racemic mixture. (a) Results for 10%, 15%, and 20% cross-link density, and (b) for 8% cross-linked network. Arrows represent the moment of deposition of the racemic droplet onto the network.

both 10 and 8% cross-linked elastomers one also finds great instability and high amplitude of alternating pitch as the network becomes increasingly weaker. This effect is not experimental noise, but rather reproducible oscillations with amplitude decreasing and period increasing with time, cf., two different curves in Fig. 5(b). In fact, we observe similar oscillations in many situations of deswelling liquid crystalline elastomers. Although no full theoretical explanation exists, we attribute this effect to nonuniform distribution (in space and time) of coupled solvent density and local nematic order.

The physical trend is clear: at low cross-linking density, the selectivity is weak; highly cross-linked networks simply cannot swell very much. How can we quantify these measurements, which unambiguously demonstrate the stereo-selectivity of imprinted cholesteric networks? Directly applying the model [12] is impossible because even a small proportion of nonmesogenic dopant reduces the local order parameter and thus affects practically all model parameters. An extension of theory is necessary to incorporate these effects, which is a part of a forthcoming publication, also presenting a number of experimental details [such as the variation of order parameter $Q(T, \phi)$, swelling kinetics and inhomogeneous network deformations on swelling/drying]. Here we simply quote the measurements of the total weight intake of the solvent. Assuming that only the left-handed component of the solvent is retained (nothing to stop the molecules with "wrong" chirality to evaporate), the figures give an idea of the stereo-separation efficiency. The 20% cross-linked imprinted network retains 5.7 wt % of 2(*S*)-bromopentane; the 15% network, 5.3 wt %; the 10% network, 4.7 wt %; and the 8% network, 4 wt %; see Fig. 6.

In Summary, we have experimentally demonstrated the topological imprinting of phase chirality in liquid crystalline polymer networks. The imprinting efficiency depends on the chiral order parameter $\alpha = \xi q_0$, a function of elastic constants K_2 and D_1. A spectacular property of imprinted networks is their capacity to preferentially absorb and retain right or left molecules from a racemic solvent. The subsequent release of the chiral solvent component is easily achieved by bringing the cholesteric elastomer into the isotropic phase, when no phase chirality remains to provide the bias, or alternatively—by stretching the rubber, which results in the helix unwinding. We did not demonstrate this explicitly in this short Letter [although Fig. 4(b) gives an indication of reversibility]. It should suffice to reassure the reader that all stereo-selectivity results were completely reproducible and reversible, after a sample was annealed into the isotropic phase. This makes the described phenomenon a practical possibility for many applications.

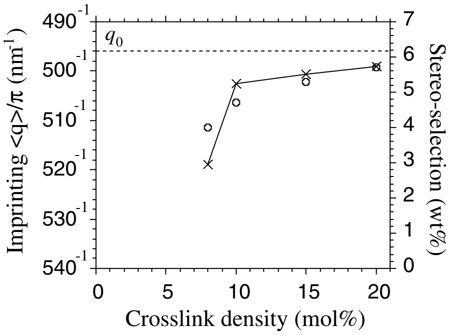

FIG. 6. The comparison between the values of inverse pitch in the imprinted networks of different cross-link density (×) and the weight percent of the amount of (*S*) component extracted by these networks from a racemic mixture (○).

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