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# Molecularly Imprinted Cholesteric Materials for Enhanced Enantiomeric Separation

Guillaume Palaprat<sup>a</sup>, Anne-Françoise Mingotaud<sup>a</sup>, Dominique Langevin<sup>b</sup>, Monique Mauzac<sup>a</sup>, Jean-Daniel Marty<sup>a,\*</sup>

<sup>a</sup> IMRCP, CNRS UMR 5623, University of Toulouse, Université Toulouse III - Paul Sabatier, 31062 Toulouse, France.

<sup>b</sup> Laboratoire Polymères, Biopolymères, Membranes, Université de Haute Normandie, UHN/CNRS, boulevard Maurice de Broglie, F-76821 Mont Saint Aignan, France

\* Corresponding author, e-mail: jean-daniel.marty@univ-tlse3.fr

## Abstract

A cholesteric network exhibiting two levels of chirality, i.e. a macroscopic chirality issued from cholesteric structure and a local chirality generated by the presence of chiral imprinted sites, was synthesized. The specific role of each level of chirality in enantio-recognition phenomena was investigated in gaz phase by comparing their sorption properties towards two enantiomers of a chiral amine. Both levels of chirality improves the separation, the chiral environment having a lower effect than the presence of chiral-specific molecular cavities.

## Highlights

- Liquid crystalline polymers with two level of chirality, i.e. molecular and supramolecular, were synthesized
- Both levels of chirality improve the enantio-recognition of a chiral amine
- Recognition is mostly promoted by the presence of molecularly imprinted sites

## Introduction

Design and synthesis of chiral macro- and supramolecular systems has promoted great interest in their relationship with biological phenomena and in their potential applications in materials science, for instance as optically active materials, catalysts, adsorbents or chiral selectors for enantiomeric separation.[1] In most of the materials used for separation, chiral discrimination originates from asymmetric affinity on a molecular scale. The materials are obtained either by grafting chiral molecules onto an achiral substrate [2,3] or, in order to improve specificity, by forming chiral cavities around a pure enantiomer into a polymer matrix to synthesize so-called molecularly imprinted polymers (MIPs).[4-9] Other materials take advantage of chiral interactions at a supramolecular scale.[10,11] Indeed, three dimensional networks can exhibit a memory function which relates to the configuration of the polymer chains at the points of crosslinking. So, de Gennes first suggested that a helical macroscopic symmetry should be introduced by simply generating the polymer network in an oriented chiral solvent. The originally achiral polymer should remember the induced chirality after removing the solvent.[12] Likewise, Hasson and coll. showed that a chiral structure could be imprinted by cross-linking an achiral liquid

crystalline polymer in the presence of a low molecular weight chiral mesogen. The liquid crystalline material retained a helical structure after extracting the dopant solvent, owing to the orientation imposed on the mesogenic side-groups by the chiral mesophase and the coupling between the mesogenic side-groups and the polymer backbone.[13] These cholesteric networks, with a chiral structure but without molecular chirality, are able to discriminate between two enantiomers.[14-16] This separation is greatly improved by adding functional groups interacting with the chiral molecules to be separated.[17]

In the present work, we propose to combine the two previous molecular and supramolecular approaches. A cholesteric imprinted network was synthesized, as described in the Figure 1, around a pure enantiomeric chiral template. Acid groups are introduced within as functional moieties. The network thus exhibits both local chirality, from the micro-cavities formed by the imprinted sites and macroscopic chirality, due to the cholesteric structure. In order to analyse the specific role of each level of chirality, the sorption characteristics were compared to those obtained with different reference networks.

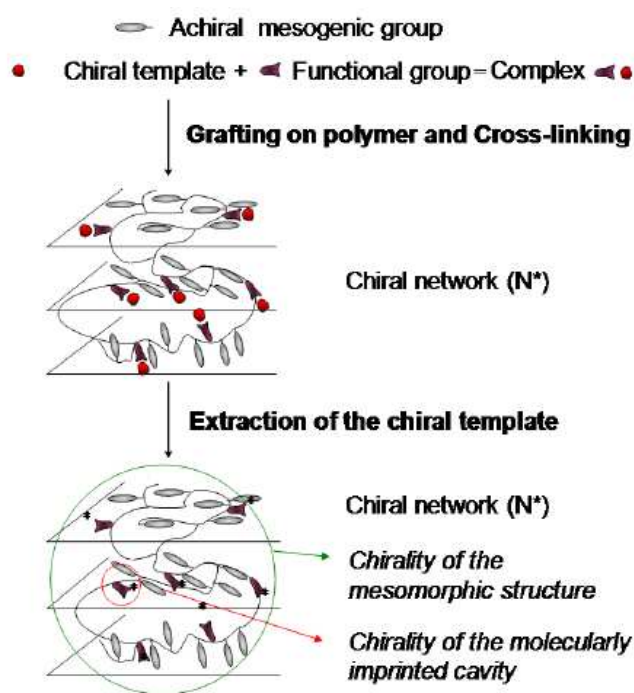


Figure 1. A. General procedure used to synthesize imprinted cholesteric network showing the two levels of chirality.

## Results and discussion

### 2.1. Synthesis and characterization of chiral materials with multi-scale chirality.

In order to obtain a network with two levels of chirality, R- $\alpha$ -methylbenzylamine is chosen as a chiral template. A liquid crystalline siloxane network is synthesized around it, as presented in Figure 2. The name of network **R-MIP-FChol** was chosen to indicate that i) its synthesis used R-enantiomer as a chiral template (**R**), ii) a molecularly imprinted polymer is obtained (**MIP**) and iii) a cholesteric network bearing functional carboxylic acid units is obtained (**FChol**)

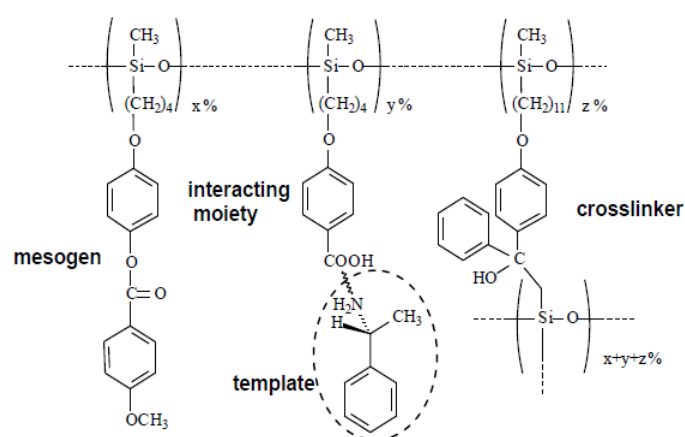


Figure 2. Chemical structure of the elastomer synthesized around the R enantiomer of the  $\alpha$ -methylbenzylamine (**R-MIP-FChol**).

R- $\alpha$ -methylbenzylamine was first complexed by 4-(3-butenyloxy)benzoic acid in toluene at 70°C for 4 hours, in order to ensure acid/amine complexation. Poly(methylhydrogenosiloxane) (90 mg ie 1.5 mmol of silane fonctions, DPn = 80), vinyl-terminated 4-(butenyloxy) phenyl 4-methoxybenzoate liquid crystalline group, and 4-(10-undecenyloxy)benzophenone as photoreactive crosslinker, [17] were incorporated into this solution (composition given in Table 1). In the presence of  $[(C_2H_5)_2S]_2PtCl_2$  (245  $\mu$ L of a 25 mg/mL toluene solution), a hydrosilylation reaction was run at 60°C for 72 hours between the silane functions and the different vinyl end groups leading to the formation of functionalized polymer. After solvent removal, the polymer was spread on a glass strip treated beforehand with a polyvinyl alcohol (PVA) solution (2 w%) and exposed to UV-lighting for 2 hours to allow cross-linking. The targeted cross-linking rate of 5% enables to maintain the organization of the network even after extraction of the amine while allowing to keep a liquid crystal material at room temperature [9]. Material was washed with water to remove remaining PVA. Films of 200  $\mu$ m thickness were thus obtained. Ungrafted groups were further extracted with acetonitrile until UV absorbance completely disappeared in the supernatant solution.

Acetonitrile is a poor solvent of the final network (swelling ratio c.a. 1.1) and therefore enables to avoid the disruption of material organization. After drying under vacuum, the **R-MIP-FChol** network was finally obtained.

Analysed by scanning electronic microscopy (SEM), the different networks present dense structures with no apparent macro or micro porosity (in the limit of SEM resolution) which is indeed expected considering the liquid crystalline nature of the studied networks. As reported in Table 1, the obtained network presented a glass transition temperature at 8°C and a cholesteric mesophase up to 68°C as demonstrated by differential scanning calorimetry, SAXS and circular dichroism measurements (Figure S1). Hence, X-ray experiments only presented a diffuse ring at 4.5 Å, typical of the nematic (N) or cholesteric phase (N\*) without any lamellar organization (Figure S1). Circular dichroism (CD) measurement was performed to assess the chiral nature of the polymer network. A reflection band due to the selective reflective properties of the cholesteric mesophase and another one due to the absorbing groups (for benzophenone, the maximum wavelength absorption was around 335 nm, and it was around 260 nm for liquid-crystalline moieties is clearly seen. In the absence of a planar texture, the first one is broadened, indicating the random distribution of the chiral domain and proving their chiral nature (Figure S2). [13] This cholesteric structure is induced by the presence of R- $\alpha$ -methylbenzylamine that acts as a chiral dopant. After its removal through washing steps, the network retained its cholesteric character as demonstrated from circular dichroism measurements thanks to the crosslinked process.

The local chirality is ensured by the conformation of functional group around R- $\alpha$ -methylbenzylamine during the formation of the network.

Two reference non imprinted materials, i.e without local chirality, were obtained by using a chiral dopant that does not interact with carboxylic function like cholesteryl acetate (10 wt.%).[14] The first one, possessing the same chemical composition as **R-MIP-FChol** networks was formed in the absence of R- $\alpha$ -methylbenzylamine molecule and is called **NIP-FChol** (NIP is for non-imprinted polymer). This network exhibited a cholesteric mesophase up to 70°C but no local chirality. Another cholesteric network with no local chirality was also synthesized by removing functional carboxylic groups during synthesis. This network called **NIP-Chol** exhibited a cholesteric mesophase up to 71°C.

A last reference network with no functional group, no liquid crystalline moiety and without any dopant, i.e not imprinted, was also prepared (**NIP**). It presents a glass transition temperature at -10°C but as expected no liquid crystalline behavior.

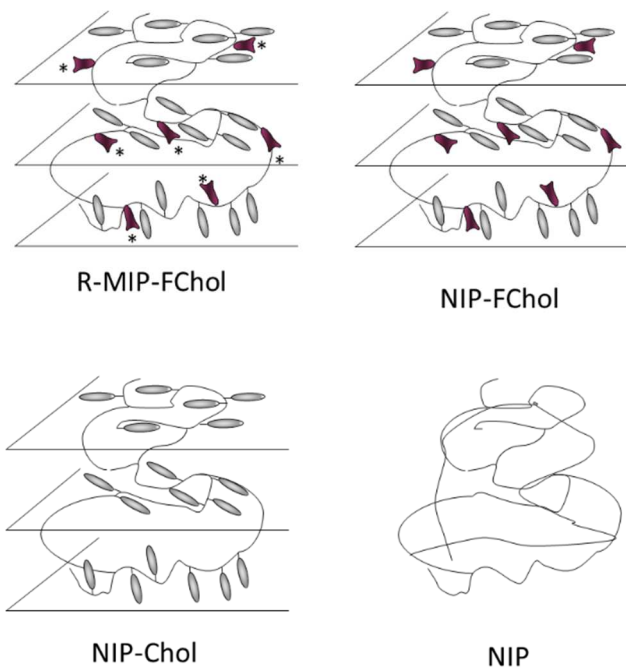
To summarize, **R-MIP-FChol** presents two levels of chirality, **NIP-Chol** and **NIP-Chol** are cholesteric networks with 0 local chirality and **NIP** has no chirality. The composition and characterization (by means of DSC, circular dichroism and small angles X-Ray diffraction measurements) of these four

different networks are given in **Table 1**. Their structures is schematically represented in **Figure 3**.

**Table 1.** Characteristics of the Samples.

Network	Molecularly imprinted	Liquid crystalline	Functionnalized acid groups	Chiral dopant	composition <sup>a</sup>			thermal properties <sup>b</sup>	
					x (% mol)	y (% mol)	z (% mol)	T <sub>g</sub> (°C)	N*→I (°C)
R-MIP-FChol	Yes (R)	Yes	Yes	Yes	87	8 <sup>c</sup>	5	8	68
NIP-FChol[17]	No	Yes	Yes	Yes	87	8	5	6	70
NIP-Chol[14]	No	Yes	No	Yes	95	0	5	6	71
NIP	No	No	No	No	0	0	100	-10	/

<sup>a</sup> x: % mol of mesogen, y: % mol of interacting moiety, z: % mol of crosslinker <sup>b</sup> T<sub>g</sub>: glass transition temperature; N\*: cholesteric phase (demonstrated by circular dichroism measurements); I/ Isotropic phase. <sup>c</sup> amount of complex with chiral template used during synthesis.



**Figure 3.** Schematic structures of the four studied materials (R: imprinted around R- $\alpha$ -methylbenzylamine, MIP: molecularly imprinted polymer, NIP: no-imprinted polymer, FChol: cholesteric network bearing carboxylic acid function, Chol: Cholesteric network)

## 2.2 Sorption properties.

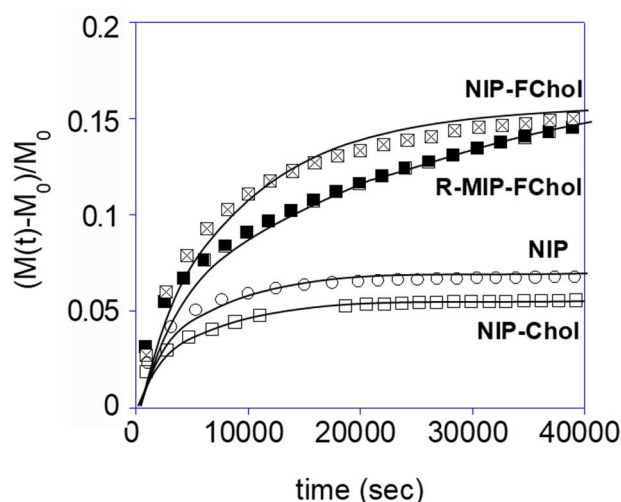
The sorption properties of the different materials were studied at 60°C by using an electronic microbalance (see experimental setup in **Figure S3**).[14] The materials were cut in two parts, each of them being used for only one of the two enantiomers of  $\alpha$ -methylbenzylamine. Prior to sorption experiments, studied networks were purged, by circulating pure nitrogen, during two days until obtaining a constant weight. By this way, remaining volatile molecules were extracted from the material. Then, the amine vapor was admitted inside the reactor and diffused in the polymer network. As the adsorption of R- $\alpha$ -methylbenzylamine in the different materials is likely to modify their organization and thus may compromise the cholesteric character of the networks, DSC and X-ray measurements were prior performed to assess the mesomorphic nature of the studied networks in presence of increasing amount of amine (up to 30%). The mesomorphic properties of cholesteric network were maintained up to 25% of adsorbed amine versus the initial polymer mass.

As illustrated in **Figure 4**, the microbalance recorded the weight variation as a function of time. The sorption kinetics could be represented by the variation versus time, of the R or S sorbed penetrant concentration  $m(t) = (M(t) - M_0) / M_0$ ,  $M(t)$  being the sample weight at time  $t$  and  $M_0$  the dry sample weight. From each of the sorption kinetics determinations, we evaluate the maximum quantity of amine  $m(\infty)$  ( $m(\infty)_R$  or  $m(\infty)_S$  for R and S enantiomer respectively) which can be sorbed by the polymer for a given vapor activity ( $a$ ) of the amine (in this study  $a_{\text{amine}} = 0.18 \pm 0.002$ ). These values are reported in **Table 2**. In the case of **NIP** samples, the curve present a plateau from which a value  $m(\infty)$  equal to 5.8 % of the initial polymer mass is measured. No real plateau was reached for the liquid crystalline materials (**R-MIP-FChol** and **NIP-FChol**) and  $m(\infty)$  values were roughly estimated at 3000 min. Values obtained are significantly higher than the one obtained for the reference samples and depends strongly on the adsorbed enantiomer: R enantiomer showing a higher affinity than S one. It is also noteworthy, that estimated  $m(\infty)$  values remained below 25%: therefore the sorption measurements were well carried out 60°C in the cholesteric mesophase of the sample. Moreover, the capacity of the functionalized liquid crystalline materials (around 20 % mass) is very high compared to non mesomorphous networks (around 1% in mass).[3] Indeed, in such liquid crystalline materials, the integrity of the structure only requires a low amount of crosslinker (5%) and therefore the networks obtained are prone to adsorb larger quantity of the molecule of interest.

**Table 2.** Diffusion Coefficient ( $D$ ), Maximum Sorbed Vapor ( $m(\infty)$ ) and Solubility Coefficient ( $S$ ) deduced from sorption measurements for R and S enantiomers of  $\alpha$ -methylbenzylamine.

network	diffusion coefficient ( $\times 10^9$ cm <sup>2</sup> /s) <sup>a</sup>		m ( $\infty$ ) (in percent of initial polymer mass) <sup>c</sup>		solubility coefficient (g/g of polymer)		ideal selectivity $\gamma$
	D <sub>R</sub>	D <sub>S</sub>	m ( $\infty$ ) <sub>R</sub>	m ( $\infty$ ) <sub>S</sub>	S <sub>R</sub>	S <sub>S</sub>	P <sub>R</sub> /P <sub>S</sub>
R-MIP-FChol	1.9 <sup>b</sup>	0.8 <sup>b</sup>	19.3	11.0	1.07	0.61	4.2
NIP-FChol	2.0 <sup>b</sup>	2.3 <sup>b</sup>	21.6	14.4	1.19	0.81	2.0
NIP-Chol	1.3	1.5	4.7	3.2	0.27	0.18	1.4
NIP	4.1	3.8	5.8	5.8	0.32	0.32	1.0

<sup>a</sup> Experimental error:  $2 \times 10^{-10}$  cm<sup>2</sup>/s. <sup>b</sup> Evaluated from fit of experimental points for short times (Fick model). <sup>c</sup> Obtained from values on the 'plateau' for long times for NIP1 and NIP2 or after 3000 min for all other samples. Experimental error: 0.01%



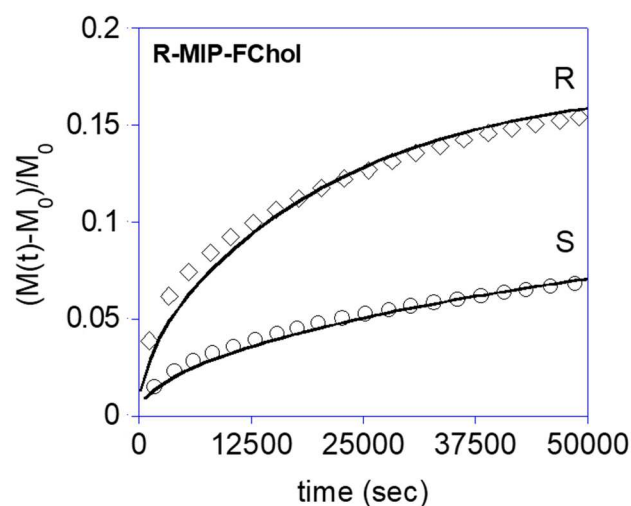
**Figure 4.** Evolution of (R)- $\alpha$ -methylbenzylamine content as a function of time, during sorption measurements, for different materials. The line represents a fit using the Fick equation (Evolution of S)- $\alpha$ -methylbenzylamine content is given in Figure S4).

These  $m(\infty)$  values are related to a solubility coefficient  $S$  ( $S_R$  or  $S_S$ ) which is representative of the levels of interaction between the polymer network and the amine enantiomer. For very dilute penetrant solutions, this coefficient is independent of the penetrant concentration and is given by Henry's law:  $m(\infty) = S \cdot a_{\text{amine}}$ . Calculated values are reported in **Table 2**.

All kinetics were also fitted by the Fick diffusion model from which a value of diffusion coefficient  $D$  can be inferred.[18,14] Whereas this model describes well the diffusion behavior of amine inside **NIP** and **NIP-Chol** networks, a deviation from Fick behavior was observed for mesomorphic functionalized networks (**R-MIP-FChol** and **NIP-FChol**). In both cases, as expected, the presence of carboxylic function renders the diffusion process more complex due to their interactions with the amine function of diffusing molecules. Nevertheless, even in these cases, sorption behavior was mainly controlled by a pure diffusion process at short times (below 40000 sec) from which the values of diffusion coefficient  $D$  ( $D_R$  or  $D_S$ ) could be extracted (**Table 2**). The diffusion coefficients for all the samples were found in the range  $10^{-9}$  cm<sup>2</sup>/s. This is in good

agreement with those measured through mesogenic materials previously studied.[14,17,19,20]

By analogy with non-porous polymer membranes, the sorption process could be described as a "solution-diffusion mechanism" and characterized by the permeation coefficient  $P$  with  $P = S \cdot D$ . [21] The ideal selectivity was then defined as the ratio of the permeability coefficients for R and S enantiomers ( $P_R/P_S$ ). Value of  $m(\infty)$ ,  $S$ ,  $D$  and ideal selectivity deduced from measurements are reported in **Table 2**. As expected, the ideal selectivity for the reference network (**NIP**) with no chirality (at a molecular or supramolecular level), was found at 1.0. The two cholesteric liquid crystalline networks with no imprinted cavities, **NIP-Chol** and **NIP-FChol**, have an ideal selectivity equal to 1.4 and 2.0 respectively. The cholesteric nature of these two networks enables to discriminate efficiently the two enantiomers. The significant improvement of selectivity observed for **NIP-FChol** was mainly explained by the presence of the acid groups, that interact with the penetrant amine molecules inducing an increase of both solubility and of ideal selectivity.



**Figure 5.** Comparison of the evolution of (R) (◊) and (S) (○) - $\alpha$ -methylbenzylamine content as a function of time (limited to short times) for **R-MIP-FChol**. The line represents a fit using the Fick equation.

Lastly, the cholesteric networks **R-MIP-FChol** comprising two level of chirality: a local chirality induced by the imprinting process and a supramolecular chirality induced by the cholesteric structure. As shown in **Figure 5**, this network present a more significant affinity for R

enantiomer than reference networks. The ideal selectivity increased up to 4.2 for this imprinted cholesteric material (**Table 2**). Therefore, enantiomeric separation is greatly amplified compared to the corresponding non-imprinted **NIP-Fchol** network. In addition, a significant decrease of both solubility coefficient and diffusion coefficient for the *S* enantiomer is observed. This could be attributed to the presence of the *R*-imprinted cavities playing against the penetration of the *S* enantiomer, or to a change of the helical structure of the cholesteric network induced by the presence of the *R* chiral template in addition to the chiral dopant during network formation. Lastly, it appears that local chirality induced by the imprinting process promotes more efficiently the enantio-recognition than the supramolecular chirality issued from the cholesteric structure (compare **NIP-Fchol** and **R-MIP-Fchol**).

## Experimental

**Reagents.** All solvents (HPLC grade) were used as received. 4-(butenyloxy) phenyl 4-methoxybenzoate, 4-(3-butenyloxy) benzoic acid, cholesteryl acetate and 4-(10-undecenyloxy)benzophenone substituents were synthesized as previously described.[22,23] 4-(butenyloxy) phenyl 4-methoxybenzoate exhibits a monotropic nematic phase at 52.2°C determined by polarized-light optical microscopy. 4-(3-butenyloxy)benzoic acid exhibits a nematic phase, from the melting point at 110.5°C and the isotropic state up to 140.1°C, as a result of dimer formation via homo-intermolecular hydrogen bonds. Polymethylhydrogenosiloxane (average number degree of polymerization of 80 units), (*S*) or (*R*)- $\alpha$ -methylbenzylamine and platinum catalyst were purchased from Aldrich Fine Chemicals.

**Apparatus.** Crosslinking was performed thanks to a xenon lamp (25 mW/m<sup>2</sup>) equipped with a high pass filter of 335 nm. Polarized-light optical microscopy (Olympus microscope equipped with a Mettler FP82HT hot stage), Differential Scanning Calorimetry (DSC, Perkin Elmer PYRIS 1 calorimeter) and X-ray experiments were used to assess the nature of the mesophases and corresponding transition temperatures. The transition temperatures given are determined on cooling from the position of the top of DSC peaks as the temperature decreased at 2°C/min; the glass transition temperatures were obtained as the temperature increased at 10°C/min. <sup>1</sup>H NMR analysis were conducted with a Bruker ARX 400 MHz spectrometer using the HRMAS accessory. The concentration of compounds in the extraction experiments was assessed thanks to a UV diode array spectrophotometer (HP 8452A). Circular dichroism measurements enable to check the chirality of obtained networks (J-815 spectrometer from Jasco equipped with a 150W Xe arc lamp light source, bandwidth of 2 nm). Amine sorption measurements have been carried out as previously described by using an electronic microbalance (IGA 001 Gas Sorption System from Hiden Analytical, Warrington, England) equipped with a humidifier module which enabled a circulation of amine with a controlled vapour pressure around the polymer sample (**Figure S3**).[14]

**Sorption measurements.** Amine sorption measurements have been carried out by the use of an electronic microbalance (IGA 001 Gas Sorption System from Hiden Analytical, Warrington, England) equipped with a humidifier module which enabled a circulation of amine with a controlled vapour pressure around the polymer sample (**Figure S3**). The humidifier module was connected to the analyser (1) containing the microbalance (resolution: 0.2  $\mu$ g). Its electronics was maintained at 55°C by a thermoregulator. In the reactor (2), thermostated at 60°C by a thermoregulated water bath, the sample was positioned in a grid pan, hung to the balance head by a long gold chain and a tungsten wire. A gas flow controller supplied a nitrogen stream (U grade from Air Liquide) which was divided into two parts A and B (controlled flow rates  $f_A$  and  $f_B$  respectively). After bubbling in a tank (3) containing the liquid amine ((*S*) and (*R*)- $\alpha$ -Methylbenzylamine) at temperature  $\theta$  (in these experiments,  $\theta = 60^\circ\text{C}$ ), stream B rejoined stream A (total flow rate:  $f_A + f_B = 200\text{ cm}^3\text{ min}^{-1}$ ) and the gas mixture circulated along the sample at atmospheric pressure. Assuming that gas B is totally saturated with amine vapor (so that vapor pressure  $p_B = \text{saturated vapor pressure } p_{\text{sat}}$  and activity  $a_B = p_B/p_{\text{sat}} = 1$ ), the vapor activity in the mixture would be equal to the ratio  $r = f_B / (f_A + f_B)$  whatever the temperature may be. However this hypothesis needed to be verified since the level of saturation of the B fluid probably depends on the bubbling conditions. The calibration of the system was thus carried out using water as vaporised liquid in the same flowing conditions (total flow =  $200\text{ cm}^3\text{ min}^{-1}$ ). A humidity sensor placed in the reactor not far from the sample allows the measurement of water activity in the A/B mixture as a function of  $r$  varying from 0 to 1. It was concluded that the vapor activity in the mixture could be linked to  $r$  with a good accuracy by the relation:  $a_{\text{amine}} = (0.90 \pm 0.01) \cdot r$ . In the amine sorption measurements, a single value of  $f_B$  was used ( $f_B = 40\text{ cm}^3\text{ min}^{-1}$ ) so that the amine activity  $a_{\text{amine}}$  can be estimated to  $a_{\text{amine}} = 0.18 \pm 0.002$  for all experiments. Before sorption measurements the sample was dried by circulating pure nitrogen ( $r = 0$ ) to a constant weight. By this way, all volatile molecules (solvent, residual low molecular weight substituents or dopant...) were expected to be extracted from the material. Then the amine vapor was admitted inside the reactor and diffused in the polymer network. The microbalance recorded the weight variation as a function of time until an equilibrium was reached.

## Conclusions

Several networks with different level of chirality, i.e. a local chirality induced by a molecular imprinting process and a supramolecular chirality related to a cholesteric structure, have been synthesized. The comparison of their sorption properties towards two enantiomers of a chiral amine showed that in the enantio-recognition phenomenon, each effect due to a chiral structure or to chiral molecular interactions improves the separation, the chiral environment having a lower effect than the presence of chiral-specific molecular cavities. A cholesteric imprinted materials was thus obtained which exhibit a very high capacity of 20 wt.% and a good ideal selectivity of 4.2. Functionalized liquid crystalline materials demonstrates

also a high capacity (around 20 % mass) compared to non mesomorphous networks (around 1% in mass).[3]

### Conflicts of interest

There are no conflicts to declare

### Acknowledgements

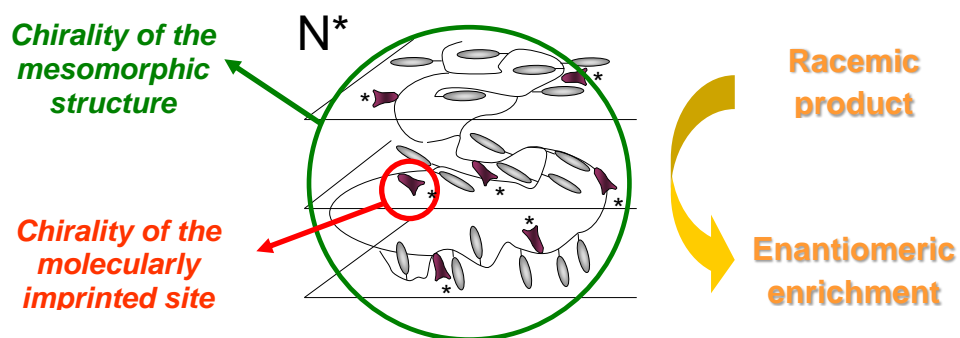
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## Graphic Content Entry



A cholesteric network exhibiting two levels of chirality was studied to assess the specific role of each level of chirality in enantio-recognition phenomena in gas phase.