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Liquid Crystals

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Liquid crystal polysiloxane networks as materials for molecular imprinting technology: memory of the mesomorphic organization

J.-D. MARTY*, M. MAUZAC, C. FOURNIER, I. RICO-LATTES
and A. LATTES

Laboratoire des Interactions Moléculaires et Réactivité Chimique
et Photochimique, U.M.R., CNRS 5623, Université Paul Sabatier,
118 Route de Narbonne, 31062 Toulouse Cedex 4, France

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A novel approach to the synthesis of molecularly imprinted polymers via non-covalent linkages has been studied. It relies on the use of thermotropic side group liquid crystal polymer networks. The polysiloxane networks obtained after extraction of the template preserved the mesomorphic organization set up in the presence of the guest molecule. A first batch rebinding analysis was performed: this study revealed that the imprinted polymer has a much greater affinity for the template molecule than has the non-imprinted polymer, and a significant selectivity.

1. Introduction

The molecular imprinting technique (MIT) is a valuable polymerization method for preparing synthetic materials able to mimic the molecular recognition phenomena present in living systems [1–3]. In this technique, a molecule (template) is associated with functional monomers to form a ‘complex’. A crosslinker is added and the polymerization/crosslinking reaction is performed around the complex. Upon removal of the template species, functionalized cavities, that have memorized the spatial features and bonding preferences of the template, are left inside the polymer network. These imprinted materials are used as chiral stationary phases in chromatography [4], as sensors in detecting devices [5], as well as materials for stereoselective reactions or as catalysts [6–8].

Most of the drawbacks in MIT have been linked to the need for a large amount of crosslinking agent (usually around 80–90%) to restrict distortion phenomena of the polymer backbones [1, 9]. The resulting stiffness of the network hinders the mechanisms of extraction and reinsertion of the template in the imprinted cavities and drastically decreases the capacity of the material [1]. Various ‘surface imprinting’ materials [10] have been proposed to solve some of these problems, but their capacities are very low.

In order to soften the network while preserving the memory of the template, the use of liquid crystal networks in MIT should be a useful tool. Mesomorphous

networks have already been used as reaction media [11] or as supports for high performance liquid chromatography (HPLC) [12]. In such systems, the interactions that developed between mesogenic moieties conferred a stiffness on the network through non-covalent reversible interactions [13]. Moreover any manifestations of the interaction between the polymer backbone and the mesogenic side groups could be transmitted to the macroscopic level providing that chemical crosslinks are introduced between the polymer backbones to form liquid crystal elastomers. Such behaviour was predicted by de Gennes [14] and subsequently a number of phenomena have been observed experimentally, including electrically-induced shape changes [15], strain-induced switching [16] and memory effects [17, 18]. The effect of crosslinking biases the structure towards the backbone configuration present at the time of network formation; any distortion of this configuration is opposed by the elasticity of the network. Consequently, such materials should display a memory of both backbone anisotropy and (by virtue of coupling) side group director orientation. As a result, in such liquid crystal materials used as molecular imprinting polymers (MIP), the template should be extractable without losing the imprinted information even with low crosslinking ratios. Larger amounts of template could then be introduced and they would be easily extracted by use of a solvent that swells the network or by heating the network above the liquid crystal/isotropic transition.

In a previous study, several liquid crystal imprinted materials, based on covalent linkages between template and MIP, were synthesized and gave some encouraging

* Author for correspondence
e-mail: docrista@ramses.ups.tlse.fr

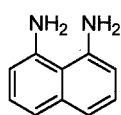
perspectives [19]. For that purpose we chose side group liquid crystal polysiloxanes in which mesogenic units were fixed end-on to the polymer backbone. These materials remained mesomorphous even in the presence of high amounts of template ($350 \mu\text{mol g}^{-1}$ of polymer). The mesomorphous behaviour increased the interactions between the polymer backbones and allowed the quantity of cross-linker to be only 10%. The molecular trapping capacity of the network ($150 \mu\text{mol g}^{-1}$ of polymer) was shown to be much greater than that of the previously studied systems (less than $100 \mu\text{mol g}^{-1}$ of polymer). Moreover, the imprinted network showed a high specificity, with 40% of the sites able to take up the template molecule.

In this present work, the template is in interaction with the mesomorphous polymer via hydrogen bonding. 1,8-Diaminonaphthalene, theophylline, and *N*-carbobenzyloxy-L-phenylalanine (figure 1), which have been used in previous studies with polyacrylate imprinted networks [20–22], were chosen as templates. The mesomorphous properties of the resulting imprinted networks were analysed, and in the case of 1,8-diaminonaphthalene, a batch rebinding study was performed in order to underline the potential value of these materials.

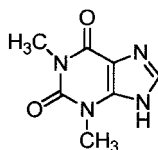
2. Experimental

2.1. Reagents and apparatus

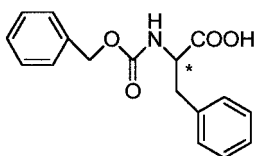
Hydroquinone, *p*-anisic acid, 4-(dimethylamino)pyridine (DMAP), 4-hydroxybenzoic acid, sodium and potassium hydroxides, Aliquat 336, poly(methyl hydrogen siloxane) (average number degree of polymerization of 80 units), *N*-benzyloxycarbonyl-L-phenylalanine (*N*-Cbz-L-Phe-OH), 1,5-diaminonaphthalene (1,5-NH₂), 1,8-diaminonaphthalene (1,8-NH₂), theophylline (theo), and 4-cyanobenzoic acid were purchased from Aldrich Fine Chemicals (Saint Quentin Fallavier, France). *N,N'*-Dicyclohexylcarbodiimide (DCC), and 1,21-docosadiene were from Fluka (Saint Quentin Fallavier, France).



1,8 diaminonaphthalene
(1,8-NH₂)



Theophylline
(theo)



N-benzyloxycarbonyl-L-Phenylalanine
(*N*-Cbz-L-Phe-OH)

Figure 1. Structures of the different templates used.

4-Bromo-1-butene was from Lancaster (Bischheim, France), dichloro(dicyclopentadienyl)platinum(II) (CpPtCl₂) was from Strem Chemicals (Newsburyport, USA), and solvents (HPLC grade) were from SDS (Peypin, France).

The nature of the mesophases and the temperature at which they occur were determined by polarized-light optical microscopy (Olympus microscope equipped with a Mettler FP82HT hot stage), differential scanning calorimetry (DSC) using a Perkin-Elmer PYRIS 1 calorimeter, and X-ray scattering experiments. X-ray measurements were performed using CuK_α radiation from a 12 kW rotating anode X-ray generator. A flat pyrolytic germanium (111) monochromator delivered a $1 \times 0.9 \text{ mm}^2$ beam to the sample. The scattered radiation was collected on a two-dimensional detector purchased from Mar Research (Hamburg). The detector system was an imaging plate (Fuji Photo Film Co. Ltd) read by scanning with a He-Ne laser. The diameter of the circular plate was 180 mm, and the pixel size $150 \times 150 \mu\text{m}^2$. The intensity map was stored as a $1200 \text{ pixel} \times 1200 \text{ pixel}$ numerical image on a Silicon Graphic station. The sample-to-detector distance was 450 mm through helium in order to lower absorption and diffusion. The smectic A (SmA) structure was established by X-ray measurements taken on samples macroscopically oriented by mechanical stress. The transition temperatures recorded in table 1 correspond to those determined from the position of the tops of DSC peaks as the temperature fell at 2°C min^{-1} ; the glass transition temperatures (T_g) were obtained as the temperature increased at $10^\circ\text{C min}^{-1}$.

¹H and ¹³C NMR analyses were conducted with a Bruker ARX 400 MHz spectrometer using the HRMAS accessory for networks. Infrared measurements were made using a Perkin-Elmer FTIR 1600. A Hewlett Packard UV diode array spectrophotometer (HP 8452A) was used to determine the concentration of the removed template in the experiments on the extraction of the template and rebinding.

2.2. Synthesis of the mesogenic substituents

The synthetic routes to the side groups grafted onto the polymer backbone are shown in figures 2 and 3.

2.2.1. 4-(3-Butenyloxy)phenol (I)

Hydroquinone (91 mmol), potassium hydroxide (91 mmol) and Aliquat 336 (50 mg) were dissolved in 80 ml of water. 4-Bromo-1-butene (74 mmol) was added dropwise and the solution heated under reflux for 24 h. The product was extracted into diethyl ether ($2 \times 100 \text{ ml}$), washed with water ($3 \times 100 \text{ ml}$) and dried over MgSO₄. The crude product was purified by chromatography on a silica gel column using CH₂Cl₂ as eluent. A brown oil was obtained (45 mmol); yield 60%. Mass: m/z 164 [M]⁺. Elemental analysis: found

Table 1. Characteristics of the samples. T_g = glass transition temperature; ΔC_p = calorific capacity variation; M = mesophase; I = isotropic phase; N = nematic mesophase; SmA = smectic A mesophase; ΔH = enthalpy variation for phase transition; d = layer spacing of the smectic A phase.

Network	Composition				Glass transition		Polymorphism		
	Template	R	x ^a mol %	y ^a mol %	$T_g/^\circ\text{C}$	$\Delta C_p/\text{J g}^{-1} \text{K}^{-1}$	I → M/ $^\circ\text{C}$	$\Delta H_{I-M}/\text{J g}^{-1}$	$d/\text{\AA}$
A ₀	—	OCH ₃	87	8	6.0	0.26	I 73.0 N	0.94	/
A ₁	N-Cbz-L-Phe-OH	OCH ₃	87	8	8.8	0.14	I 67.9 N ^b	0.90	/
A ₂	theo	OCH ₃	87	8	8.2	0.22	I 64.2 N	0.32	/
A ₃	1,8 NH ₂	OCH ₃	87	8	8.6	0.15	I 69.9 N	0.78	/
B ₀	—	OCH ₃	79	16	10.5	0.20	I 71.9 N	0.80	/
B ₁	N-Cbz-L-Phe-OH	OCH ₃	79	16	10.0	0.28	I 71.2 N ^b	0.45	/
B ₂	theo	OCH ₃	79	16	6.2	0.17	I 54.5 N	0.29	/
C ₀	—	CN	87	8	27.7	0.13	I 129.8 SmA	0.95	36.4
C ₁	N-Cbz-L-Phe-OH	CN	87	8	28.3	0.20	I 129.6 SmA	0.60	34.5
C ₃	1,8 NH ₂	CN	87	8	16.8	0.13	I 124.3 SmA	1.00	36.5
D ₀	—	CN	79	16	12.1	0.4	I 116.0 SmA	2.40	34.5
D ₃	1,8 NH ₂	CN	79	16	27.5	0.10	I 105 N	<0.1	/

^a Mol % of substituents x or y linked to the polysiloxane chain. The crosslinker ratio was kept to 5 mol %. x, y, z were as defined in figure 4.

^b Nematic or cholesteric mesophase (not yet determined).

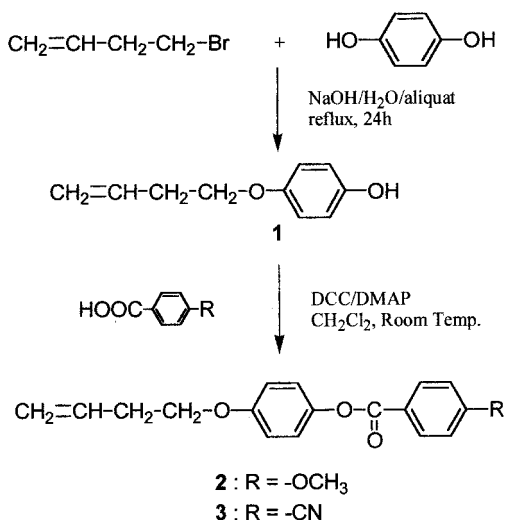


Figure 2. Scheme of synthesis of the mesogenic moieties **2** and **3**.

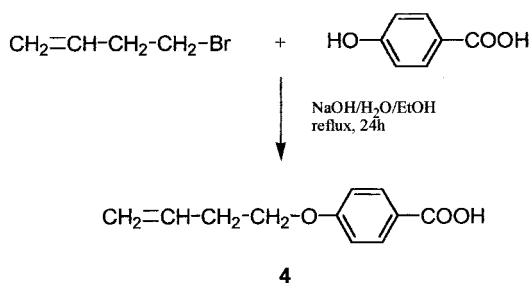


Figure 3. Scheme of synthesis of 4-(3-butenyloxy)benzoic acid.

(calculated) H 7.20 (7.31), C 73.34 (73.17)%. ¹H NMR (400 MHz, CDCl₃, δ ppm): 2.50 (m), 4 (t), 5.2 (m), 5.8 (m), 6.8 (s). ¹³C NMR (62.9 MHz, CDCl₃, δ ppm): 33.7, 68.1, 115.9, 117, 134.5, 149.5, 153.

2.2.2. 4-(3-Butenyloxy)phenyl 4-methoxybenzoate (**2**)

4-(3-Butenyloxy)phenol (64 mmol), *p*-anisic acid (66 mmol), DCC (77 mmol), and DMAP (5 mmol) were dissolved in dichloromethane and the resulting solution stirred overnight at room temperature. The mixture was filtered, evaporated, and the product recrystallized twice from ethanol. The ester **2** was obtained as white crystals, yield 80%.

As shown by optical microscopy and DSC, this compound exhibits a monotropic nematic phase: melting point 92°C, isotropic to nematic phase 52°C (enthalpy variation, $\Delta H_{I-N} = 1.87 \text{ J g}^{-1}$). Mass: m/z 298 [M]⁺. Elemental analysis: found (calculated) H 6.05 (6.04), C 71.48 (72.48)%. ¹H NMR (400 MHz, CDCl₃, δ ppm): 2.2 (t), 2.5 (m), 4 (t), 4.7 (d), 5.1 (m), 5.9 (m), 6.9, 7.1, 7.5 and 8.2 (d). ¹³C NMR (62.9 MHz, CDCl₃, δ ppm): 33.6, 64.5, 67.6, 117, 115.2, 122.4, 126.5, 129, 128.7, 134.3, 144.4, 146.7, 156.6, 171.8.

2.2.3. 4-(3-Butenyloxy)phenyl 4-cyanobenzoate (**3**)

The same experimental procedure as for **2** was used except that 4-cyanobenzoic acid was introduced instead of *p*-anisic acid. **3** was obtained as white crystals, yield 80%. As shown by optical microscopy and DSC, this compound exhibits a monotropic nematic phase: melting

point 90.9°C, isotropic to nematic phase 60.8°C (enthalpy variation, $\Delta H_{I-N} = 0.874 \text{ J g}^{-1}$). Mass: m/z 293 $[\text{M}]^+$. Elemental analysis: found (calculated) H 5.05 (5.11), C 73.93 (73.72), N 4.82 (4.79)%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm): 2.5 (m), 4 (t), 5.1 (m), 5.8 (m), 6.9, 7.1, 7.8 et 8.2 (d).

2.2.4. 4-(3-Butenyloxy)benzoic acid (**4**)

4-Hydroxybenzoic acid (100 mmol) was dissolved in ethanol (100 ml). Sodium hydroxide (200 mmol) and water (50 ml) were added and the solution was brought to reflux. 4-Bromo-1-butene (100 mmol) was added dropwise and the mixture heated under reflux for 24 h. The ethanol was evaporated off and the residue diluted with water (100 ml). The solution was cooled and acidified with concentration hydrochloric acid. Then the crude product was filtered off and purified by recrystallization (ethanol/water 50% v/v). **4** was obtained as white crystals, yield 40%. Due to dimerization through hydrogen bounds, this compound exhibits a nematic phase: melting point 110.5°C, isotropic to nematic transition 140.1°C (enthalpy variation, $\Delta H_{I-N} = 7.8 \text{ J g}^{-1}$). Mass: m/z 192 $[\text{M}]^+$. Elemental analysis: found (calculated) H 6.29 (6.29), C 68.88 (68.74)%. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm): 2.5 (m), 4.05 (t), 5.1 (m), 5.2 (m), 5.9 (m), 6.98 (m), 8.0 (m).

2.3. Preparation of molecularly imprinted polymers

A scheme showing an example of a synthesis is given in figure 4. In this case, 1,8-diaminonaphthalene is the template.

The template and **4** were previously mixed in toluene at 70°C for 5 h in the molar proportion of 1/4. They formed a complex through H-bonding as shown by $^1\text{H NMR}$ (shift of δ_{COOH} from 11.5 to 4.7 ppm). The complex, **2** or **3**, and the 1,21-docosadiene cross linking agent were linked to the polysiloxane chain by a one-step hydrosilylation reaction [23], between the silane functions and the different vinyl end groups, catalysed by dichloro(dicyclopentadienyl)platinum(II). In each network, the amount of crosslinking agent was kept to 5 mol % relative to the polymer units. The products from **4**, **2** or **3**, and 1,21-docosadiene exhibits thermotropic mesomorphic behaviour: with **2**, melting point 85°C, isotropic to monotropic nematic phase 53°C; with **3**, melting point 86°C, isotropic to monotropic nematic phase 62°C. Reagents, catalyst and toluene were added to the complex solution in a Teflon® mould and the mixture was kept at 50°C for 96 h. The concentration of the final polymer chains was set at 37 vol % in order to perform the reaction above the gel point [23]. The preservation of the mesomorphic behaviour of the samples at this high concentration was checked by X-ray experiments. This result confirmed previous studies

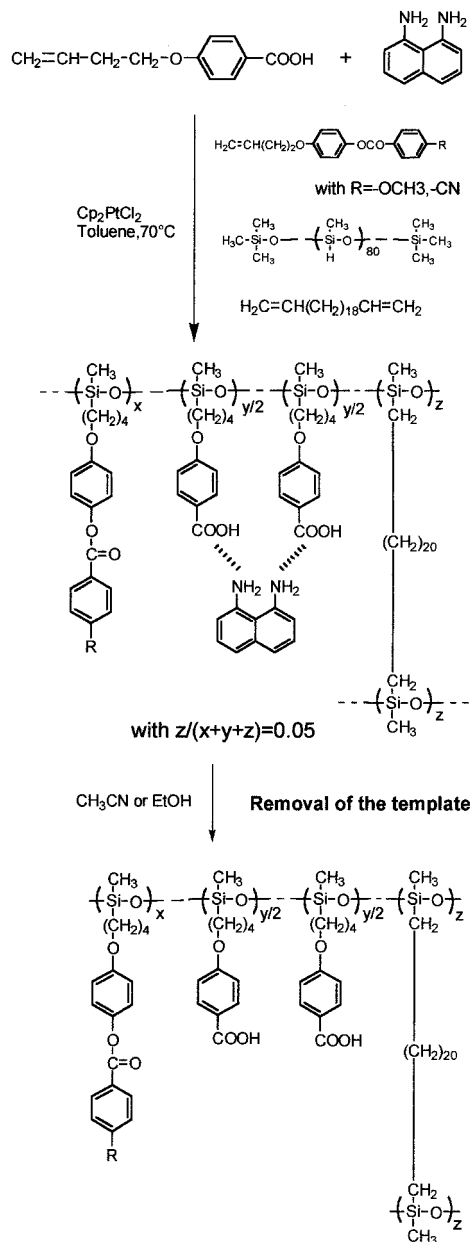


Figure 4. Schematic illustration of the molecular imprinting procedures.

made on similar samples [24]. So all the samples were crosslinked in their thermotropic nematic or smectic phase. At the end of the reaction, the solvent was slowly evaporated over four days to avoid damage such as holes or cracks inside the materials. The samples obtained were in the form of circular membranes (diameter about 20 mm, thickness $0.6 \text{ mm} \pm 0.01$). Scanning electron micrography (SEM) of the imprinted membrane shows a homogeneous structure with no macroscopic porosity.

Four series of imprinted networks, differing in chemical composition, were synthesized as reported in

table 1. In each series, different templates were used as shown in figure 1. Corresponding reference networks (A_0 , B_0 , C_0 , D_0) were prepared with exactly the same procedure except that no template was used.

The absence of the Si–H stretching vibration band at 2160 cm^{-1} in the FTIR spectra, and of the corresponding ^1H NMR peak at 4.7 ppm, showed that no unsubstituted silane functions remained in the final networks. The proportion of the substituted silane functions x and y (figure 4), checked by ^1H HRMAS NMR spectroscopy, was in good agreement with the introduced amount of **2** and **4**.

The template was extracted at room temperature with a large volume of polar solvent, until the UV absorption due to the template was negligible in the washing solution (see §3.1). Acetonitrile was used as extraction solvent for samples A and B but could not be used for samples C and D due to the interactions that arise between the cyano groups of **3** and acetonitrile which disrupt the mesomorphic behaviour. In these cases ethanol was used.

At the end of the washing process, the solvent was slowly evaporated. The imprinted network was analysed by infrared spectroscopy and no signal due to the template was detected. A single-block imprinted network was obtained which could be used as a membrane in future experiments.

2.4. Swelling studies

Although the mesomorphic organization was theoretically inscribed inside the final network, the samples were prevented from swelling too much to avoid any possible distortion of the structure or damage to the material. The ability of the networks to swell in the presence of solvent was evaluated for various solvents. To quantify swelling, samples were put in a large excess of solvent and swollen to saturation. The maximum swelling weight ratios reached are reported in table 2; these are average values obtained on three samples.

Table 2. Swelling weight ratio of the networks synthesized.

Solvent	Q^a
Heptane	1.1
Acetonitrile	1.3
Chloroform	4
Ethanol	1.1
Toluene	2.5
Acetone	2.1
Diethyl ether	1.5

^a Q = Ratio of the weight of the swollen network to the weight of the dry network.

2.5. Batch rebinding analysis

Batchwise adsorption tests were conducted using the imprinted (A_3) and the reference (A_0) networks in order to assess the effectiveness of the imprint technique. A_3 or A_0 (single blocks of 200 mg) were incubated in a vial with 20 ml of a 15×10^{-6} M heptane solution of 1,8-NH₂ or a positional isomer (2,5-NH₂) at room temperature for 36 h without stirring. Subsequently, the concentration of the molecule remaining in the supernatant liquid was determined by UV measurements at 350 nm. The initial solution of template (control solution) was examined under identical conditions to check that no evolution had occurred.

3. Results and discussion

3.1. Extraction of the template and evolution of the mesomorphic behaviour

An example is given in figure 5. At the beginning of the washing process, a rapid evolution in UV-absorption in the supernatant liquid due to the release of the template, and an increase in the transition temperature of the network (about 10°C) were observed for all the materials. Then no significant variation in the latter quantity was seen, whereas template was still being removed from the network as monitored by the UV measurements. This result supports a two-step extraction mechanism. Firstly, template and liquid crystal not bound by the network are eliminated (SEM showed a deposit upon the membrane, about $20\text{ }\mu\text{m}$ thick, that disappeared after the first washing steps). This excess of template plays the role of an impurity and induces a shift in the isotropization temperature. In the second step, the template that interacts with the network is slowly extracted until the UV absorption in the solution is negligible. At the same time no evolution of the

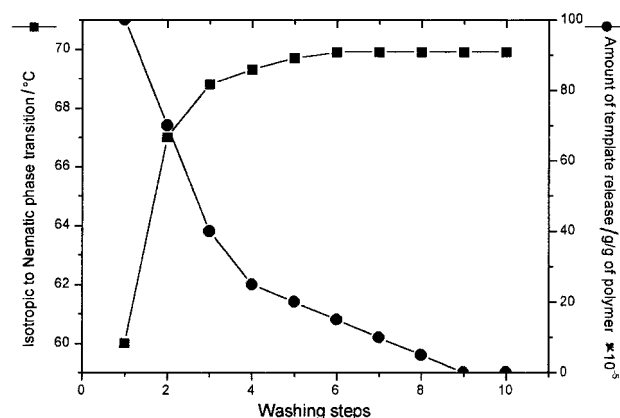


Figure 5. Extraction of the template and evolution of the mesomorphic properties during the washing process. Sample: 200 mg of A_3 network; each washing step: 20 ml of acetonitrile, 5 h, 25°C . The amount of template release is calculated from the UV absorption at 350 nm.

transition temperatures is seen, proving that the network keeps the memory of the template. After extraction of the template the imprinted network preserves the mesomorphic organization set up in the presence of this molecule.

3.2. Transition temperatures and mesomorphism of the washed imprinted networks

Results obtained from DSC and X-ray experiments, on washed imprinted networks and reference materials, are reported in table 1. All the samples presented were washed as described in §2.3 and 3.1, and only residual traces of template should have remained. As a result, differences observed between samples in the same series A, B, C or D in table 1, could not be attributed to the fact that remaining template was still present in the network.

At room temperature all the samples exhibited mesomorphous behaviour. Networks C and D₀, grafted with cyano substituents, showed the smectic A phase, while other materials had a non-lamellar phase. The layer spacing *d* of the smectic phases, determined from the X-ray Bragg diffraction, was less than twice the length of the molecule (the length of side group 3 in its most extended conformation plus the backbone thickness was about 19 Å); this corresponds to a partial bilayer structure. This layer spacing is largely independent of the template molecule. For samples A₁ and B₁, imprinted by a chiral template, the nematic or cholesteric behaviour has not yet been determined.

Transition temperature variations from those of the reference sample depended on the template used and on its concentration. The largest variations were obtained in the case of theophylline which has a structure far removed from the that of the mesogenic moieties. This results in extensive disruption of the mesomorphic order, as confirmed by the great decrease in enthalpy variation (ΔH). The higher the amount of template, the more pronounced this effect is (see comparison between A₂ and B₂ or between C₃ and D₃). This effect can induce the disappearance of the smectic A phase giving a less ordered nematic phase (sample D₃). On the other hand almost no difference was observed in the transition temperatures between reference networks and those imprinted with *N*-Cbz-*L*-Phe-*OH* which is most compatible with the mesogenic moiety. In this case the analysis of the mesomorphic behaviour is insufficiently explicit to reach conclusions about the memory effect relating to this template.

DSC experiments have shown that after heating the samples in the isotropic phase for one hour, the isotropic–nematic or isotropic–smectic phase transition remained the same even after several thermal cycles. We

can assume that transition temperatures are directly related to the three-dimensional distortion of the network. Such distortion arises from the interactions between template, 2 or 3 and 4 which can induce conformation constraints inside the networks during crosslinking. Hence, transition temperatures are a direct expression of the template effect.

In conclusion of this polymorphism study we can note the following. (i) The differences observed in the transition temperatures, in the enthalpy variations or in the lamellar structure imply that the template, even after its extraction, exerts a strong influence over the imprinted network. This is the manifestation of a significant memory effect of the template on the mesomorphic structure. The memory effect occurs even though the amount of crosslinker is low (5%). (ii) A relatively high amount of template (above 8%) can be introduced without losing the mesomorphic order. (iii) It is easy to change the nature of the mesophase or the transition temperature by varying the mesogen used. This must be adapted to the template.

We also observed that the samples have low glass transition temperatures. Therefore the networks studied here are rather flexible at temperatures below or near the room temperature. The glass transition temperature could be modulated by changing mesogen molecule (compare series A and C). Depending on the required uses, the materials can be kept in the glassy state with both a frozen mesomorphic order and a high elastic modulus or above T_g with a higher flexibility and the ability to be mesomorphous or not. In the latter case, the samples could be heated to the isotropic state, in which interactions between the template and the mesomorphic network are lowered, so that the release phenomenon should increase.

3.3. Batch rebinding studies

The first batch-rebinding studies were performed with the network imprinted with 1,8-NH₂ (A₃) and the non-imprinted network (A₀). Heptane, which is non-polar and a poor solvent of the network (see table 2), was chosen to perform this study. It causes less disturbance of the mesomorphic order and hydrogen bonding that occurs at 25°C.

The amount of 1,8-NH₂ rebound, determined from the UV absorption of the supernatant solution is reported in figure 6. It is obvious that the non-imprinted network (A₀) exhibits a significantly lower degree of template uptake compared with the imprinted network (A₃). A₀ and A₃ having the same chemical structure, these results indicate that, in addition to the hydrogen bonding or electrostatic interactions between the functional

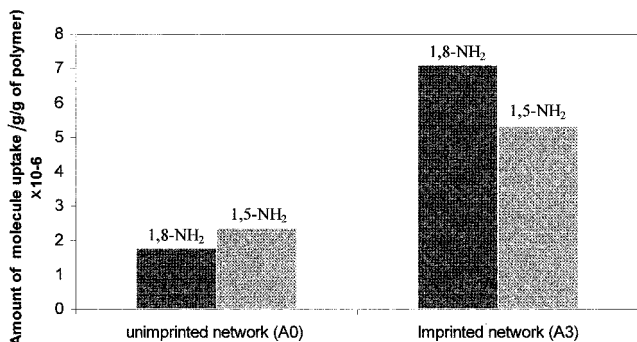


Figure 6. Batch rebinding experiments. Amount of 1,8-NH₂ and 1,5-NH₂ uptake by the non-imprinting network A₀ and the 1,8-NH₂ imprinting network A₃. Adsorption time: 36 h; initial concentration of 1,8-NH₂ or 1,5-NH₂: 15 μm in heptane, $T = 25^{\circ}\text{C}$.

groups of the polymers and the template, microcavities corresponding to the shape of 1,8-NH₂ are necessary for effective binding. Consequently the polymer gained affinity for the template through the MIT.

Substrate selectivity was also investigated under the same conditions. For this study an isomer of 1,8-NH₂ was used (1,5-NH₂). As indicated by the amount of molecule rebound (55% for 1,8-NH₂ against 30% for 1,5-NH₂), networks prepared using 1,8-NH₂ as print molecule showed higher selectivity for its complementary substrate than for a closely related compound. This demonstrates a molecule-specific imprinting effect similar to that usually observed [20].

Other studies of batch rebinding have to be made, and studies of the uptake capacity and temperature dependence of this material are also in progress.

4. Conclusion

This study has shown the potential of liquid crystal polymer networks for use as materials in molecular imprinting technology. In these novel networks, the crosslinking ratio was low. Analysis of the mesomorphic order has demonstrated a memory effect of the liquid crystal structures set up in the presence of the template that was preserved even after heating to the isotropic state. The first rebinding studies, performed in the mesomorphic phase, showed a significantly higher affinity of the imprinted material towards the template than the non-imprinted one. The liquid crystal polymer networks kept the memory of the template while preserving the flexibility of the network. Moreover, these materials exhibited a good selectivity towards the printed molecule.

It may be possible to benefit specifically from the liquid crystal character, either to orient substituents, or to modify the interactions between the network and the template, by heating to the isotropic state for example. Moreover, the use of chiral templates could induce

a chiral structure in the mesophase. This could then be retained even after the extraction of the template [25, 26], and so could improve the resolution of racemic mixtures. Lyotropic liquid crystals could also be considered.

Some questions arise from the present results, especially the precise role of the pendant mesogenic groups. Is it the liquid crystalline interactions that toughen the network and increase its selectivity, or is it the bulkiness of the pendant groups and their chemical interactions that play the main role? Experiments have to be done for the isotropic state to answer this question.

The best compromise between the proportion of the mesogenic units and the amount of template has yet to be found. Moreover, in order to optimize the conditions of use and to enhance the accuracy with which selectivity is achieved in this kind of network, chromatography studies are under consideration.

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